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**INTERFACIAL INSTABILITIES:
IMPLICATIONS FOR MULTI-MATERIAL
MOULDING**

by

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***A thesis submitted in partial fulfillment of the requirements for
the degree of Doctor of Philosophy in Engineering***

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DECLARATION

I declare that all the work described in this thesis was undertaken by myself unless otherwise acknowledged in the text and that none of the work has previously been submitted for any academic degree. All sources of quoted information have been acknowledged by means of references.

Vannessa Goodship

Abstract

This work investigates and identifies the mechanisms that are at work in the creation of instabilities during co-injection moulding. Two aspects are investigated, neither of which has been previously reported. One seeks to eliminate the instabilities, the other to control them to produce mechanical interlocking of incompatible polymeric materials. Complex rheological and thermodynamic interactions take place during the co-injection moulding of materials of different generic families, which need to be understood before successful multi material mouldings can be achieved. Moulding trials on miscible, compatibilised and immiscible polymer systems were carried out to determine processing parameter effects.

Analysis of tensile behaviour identified differences between injection moulding and co-injection moulding samples which are indicative of different heating and cooling regimes in the systems. Scanning electron microscopy analysis also assisted explanation of these effects. A previously unobserved bulk weakness in compatibilised systems was found. Surface profilometry was used to measure the size of disturbances at the wave fronts. The extent to which the interfacial instability occurs and to the material systems to which it applies was found. Instabilities were found or induced in all material systems investigated, including those where skin and core materials are the same. Mechanisms of instability at the melt front interface were determined and were found to be the result of stratification of elastic properties. Processing conditions were found to minimize instability by minimizing differences in elasticity at the interface. A novel process route using controlled instabilities was also proposed and investigated for the use of immiscible material systems. By controlling the moulding parameters, the potential problem of instability was used to provide a solution to bonding immiscible materials in co-injection mouldings without the use of compatibiliser.

ABBREVIATIONS and SYMBOLS

HDPE	High density Polyethylene
PA6	Polyamide 6
PA12	Polyamide 12
PP	Polypropylene
PS	Polystyrene
LDPE	Low density polyethylene
η	viscosity
σ	stress
$\dot{\gamma}$	shear rate
τ	shear stress
SCORIM	shear-controlled orientation in injection moulding
SEM	scanning electron microscopy
Tg	glass transition temperature

Chapter 1. Introduction

1.1 Background

Injection moulding is the most commercially important of all plastic processing methods. It allows production of intricate, high precision, three-dimensional parts at high production rates. Designers have made use of the great variety of polymer materials commercially available for this process and this has enabled plastics to replace traditional materials such as wood, glass or metal in numerous applications. e.g. plastic cutlery, plastic gear wheels [Rosato, 1986].

Injection moulding is a relatively young industry but many variants of the process have been developed such as single injection, injection-compression, gas assisted and co-injection. This thesis will concentrate on the co-injection moulding process.

Co-injection moulding is a variant of the standard injection process and has been in use since the early nineteen seventies [Oxley, 1971]. This technology offers the advantages of combining two or more material properties to produce a 'sandwich' structure. This is achieved by making sequential injections into the same mould with one material as the core and another as the skin. This is shown in Figure 1-1.

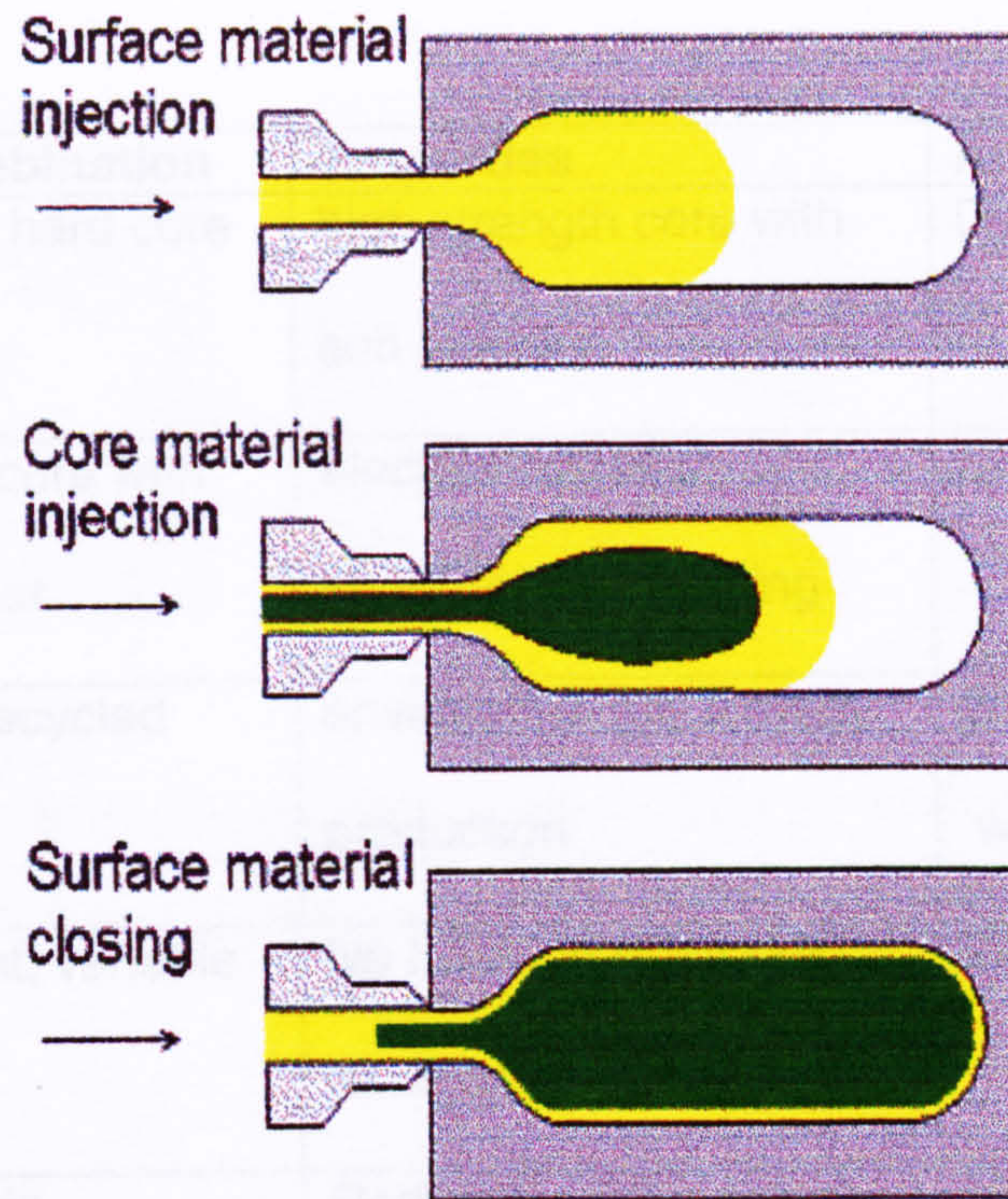


Figure 1-1 *encapsulation of core material by skin during co-injection moulding*

The co-injection moulding process entails the injection of molten plastic for the skin layer into the mould cavity. After a certain preset time, a second plastic that will make up the core is injected and for a period, there is simultaneous injection of both materials. This pushes the moving layer of skin material against the cavity walls where it cools and solidifies. The final stage of mould filling is injection of the core material only, although sometimes the mouldings are 'capped' with skin layer to complete encapsulation of the core.

Co-injection moulding offers numerous possibilities in terms of a variety of material combinations, some of which are shown in Table 1.1.

Material Combination	Properties	Application
Soft feel skin/ hard core	high strength core with soft feel skin	Door handles
Unfilled skin/ core with conductive filler	electromagnetic interference shielding	Computer housings
Virgin skin / recycled core	environmentally friendly production	Garden Furniture, wall holder
In Mould Paint, variable core	No finishing of product required after moulding	Wheel trims
pigmented skin, uncoloured core (or reverse)	Reduced pigment cost	Yogurt Pot

Table 1-1 Applications for co-injection mouldings [Zoetlief, 1995]

Three of these examples of co-injection mouldings where the skin/core interfaces can be clearly distinguished are shown in Figure 1-2.



Figure 1-2 Examples of co-injection mouldings [Ferromatik, 1996]

left: yogurt pot, centre: door handle, right: wall holder (see Table 1 for more details)

One of the most difficult technical problems with co-injection moulding is that the core material must be prevented from large scale mixing with the skin material, in order to retain a consistent skin layer thickness and resultant properties. It must also be prevented from penetrating the skin of the moulding [Stephenson, 1996]. This is controlled by changes to the speed and time of injection, polymers melt temperature and mould temperature all of which will be discussed in more detail in Chapter Two.

The process does have limitations. There is a need for the skin and core materials to be compatible with each other in terms of adhesion and shrinkage. Adhesion of the layers is necessary to prevent the core material becoming detached from the skin especially if the moulding is likely to be exposed to mechanical loads. Differences in shrinkage rates can lead to problems with warpage and moulding distortion. There are also limitations in the variation of flow characteristics between the two materials that are

permissible. Rheology plays a large part in the relative skin/ core distribution [Cogswell, 1996].

One way to overcome the difficulties of adhesion is by using a compatibiliser. Compatibilisers are polymers which when added to a blend increase the adhesion between the different materials within the blend and therefore improve the material mechanical properties. Compatibiliser use has been widely reported in producing material blends with properties superior to those of the individual polymers [Datta, 1996].

The use of compatibilisers in the core component of co-injection moulding was developed and patented by Rover [Coates, 1999]. This work was an attempt to develop cheap and paintable plastic body panels. Polypropylene is cheap but is notoriously difficult to paint due to its low surface energy [Lamborne, 1987]. By combining a nylon 6 skin with a polypropylene core it was possible to overcome the difficulties associated with painting polypropylene. The nylon 6 skin acted as a paint primer whilst keeping the panel costs down by using a polypropylene core.

This development of compatibiliser technology offers new possibilities for co-injection moulding. The materials no longer need to have adhesive properties as the compatibiliser can be used to bond the materials together. This opens wider applications for co-injection moulding by allowing commercially and economically interesting combinations of materials to be moulded. However, this system has a problem. When moulding a nylon 6 skin with a compatibilised polypropylene core, a surface distortion was

observed at the area of the interface causing a pronounced aesthetic defect [Coates, 1998]. This is shown in Figure 1-3. The source of this defect was unknown.

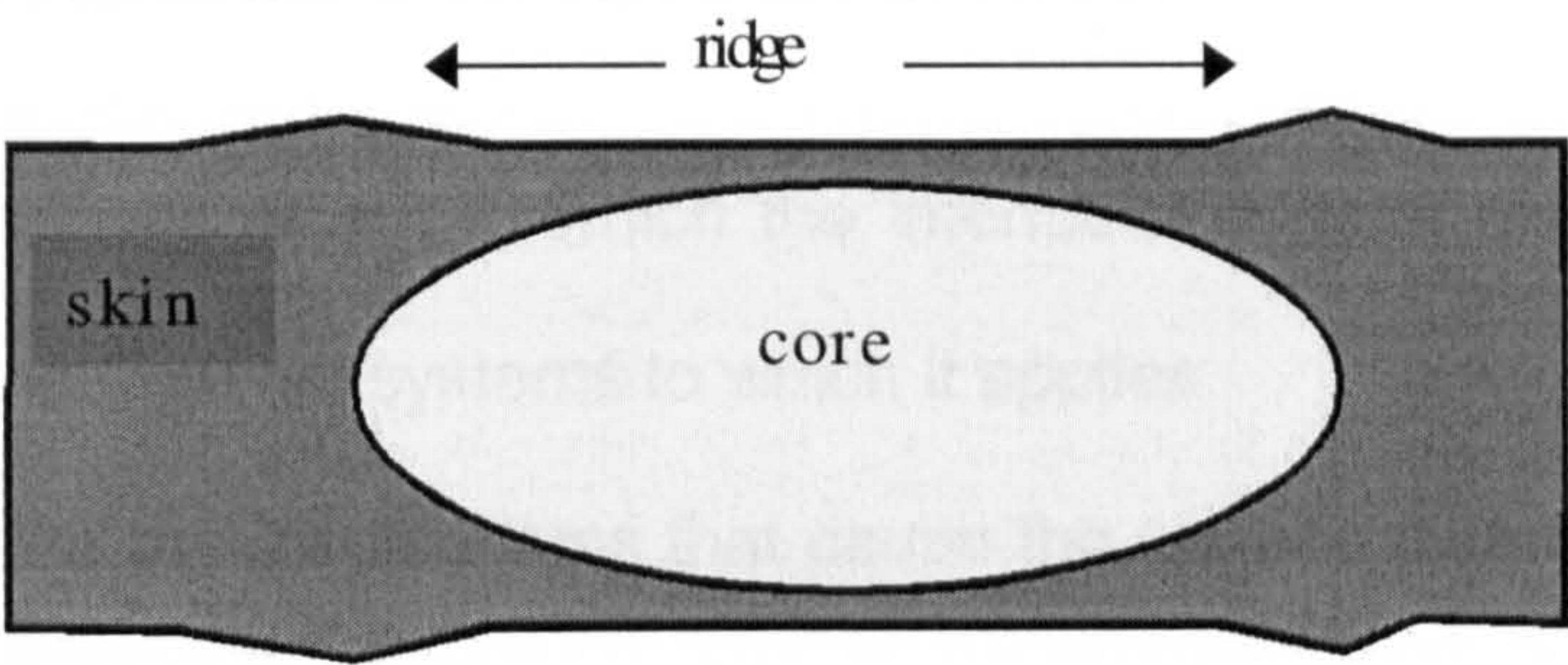


Figure 1-3 Cross section of co-injection moulding showing ridge effect at surface of skin/core moulding interface

Preliminary studies also revealed this defect visible on other material types.

1. 2 Aims of the project

Use of the compatibilised co-injection process for producing multi-material mouldings, is limited by the formation of a ridge that appears at the flow front of the core component and reads through onto the surface causing a surface distortion.

The aim of this work is to investigate and identify the mechanisms that are at work in the creation of this effect and to find a means to eliminate the problem. Complex rheological and thermodynamic interactions take place during the co-injection moulding of materials of different generic families, these need to be understood before successful multi material mouldings can be achieved.

1.3 Objectives

The overall objectives of the thesis are as follows:

1. Determine the extent to which the interfacial surface distortion extends and to the material systems to which it applies.
2. Investigate the mechanisms that cause the surface distortion at the melt front interface.
3. Determine processing conditions to eliminate the surface distortion effect.
4. Develop a process route for the use of immiscible materials that eliminates the aesthetic defect and hence removes some of the limitations in the use of various combinations of immiscible materials for moulding.

Chapter 2. Injection Moulding

2.1 Injection Moulding

It would be impossible within the scope of this work to deal comprehensively with the vast subject of injection moulding. It is one of the most common of the plastic processes and a number of books have been published on the subject [Whelan, 1984], [Whelan 1982], [Rosato 1986]. A brief overview of the general moulding process will be given before attention is turned to co-injection moulding.

The injection moulding process can be broken down into four stages:

- **Plastication**
- **Filling**
- **Packing**
- **Solidification.**

- **Plastication**

Plastication is the action of mixing and melting the feedstock. The polymer flow rate is governed by the material process conditions of the plastication stage and is a combination of material rheology, barrel temperature, shear, back pressure and screw speed. The basic aim is to produce a homogeneous and formable melt for the next stage where the material enters the mould.

- **Filling**

The parameters of mould filling are of great importance to the quality of the finished article especially when considering factors such as warpage (orientation effects) and surface finish (skin formation). Filling dynamics are also thought to be the major factor in affecting the levels of residual stress [Chiu, 1987]. It is important that injection speeds are reproducible as slight changes can cause variations in the product. Injection speeds that are too high can cause jetting and degradation and thus affect mechanical properties [Wilkinson, 1999]. A low speed may cause an increase in injection pressure requirements due to a thicker frozen layer. This is because the molten material cools at the lower speed, meaning higher pressures are required to force other material in behind it. This can produce incomplete filling of the mould often referred to as short shots.

- **Packing and cooling**

The packing stage's purpose is to add extra material to compensate for the shrinkage caused by the increasing density of the solidifying polymer. If the additional polymer were not injected the component would shrink and warp due to non uniform cooling.

Ideally the packing and cooling stages should be such that the final dimension is maintained as close as possible to design tolerances. Variables during this stage are packing pressure, packing time and the mould temperature. Bad mould design can lead to inconsistent cooling along the dimensions of the mould surface which can cause increased residual stresses which lower the mechanical properties of the part as well as causing warpage [Bushko, 1994].

2.1.1 Differential shrinkage and cooling effects

When considering a centre-fed flat plaque, it is often found that radial shrinkage will be double that in the circumferential direction, this is due to orientation effects [Berins, 1991]. Material will be orientated in the direction of flow and will shrink more in the direction of flow than perpendicular to it. Although this can be made worse by indifferent moulding techniques, it is not always possible to prevent it from occurring. This is because moulds fill in a so called 'fountain flow' pattern which is shown in Figure 2-1. The first material to enter the mould is under very little pressure as it flows into the channel, but as it proceeds towards the extremities of the mould, it is progressively cooled. The material that follows is hotter and begins to pressurize that already there.

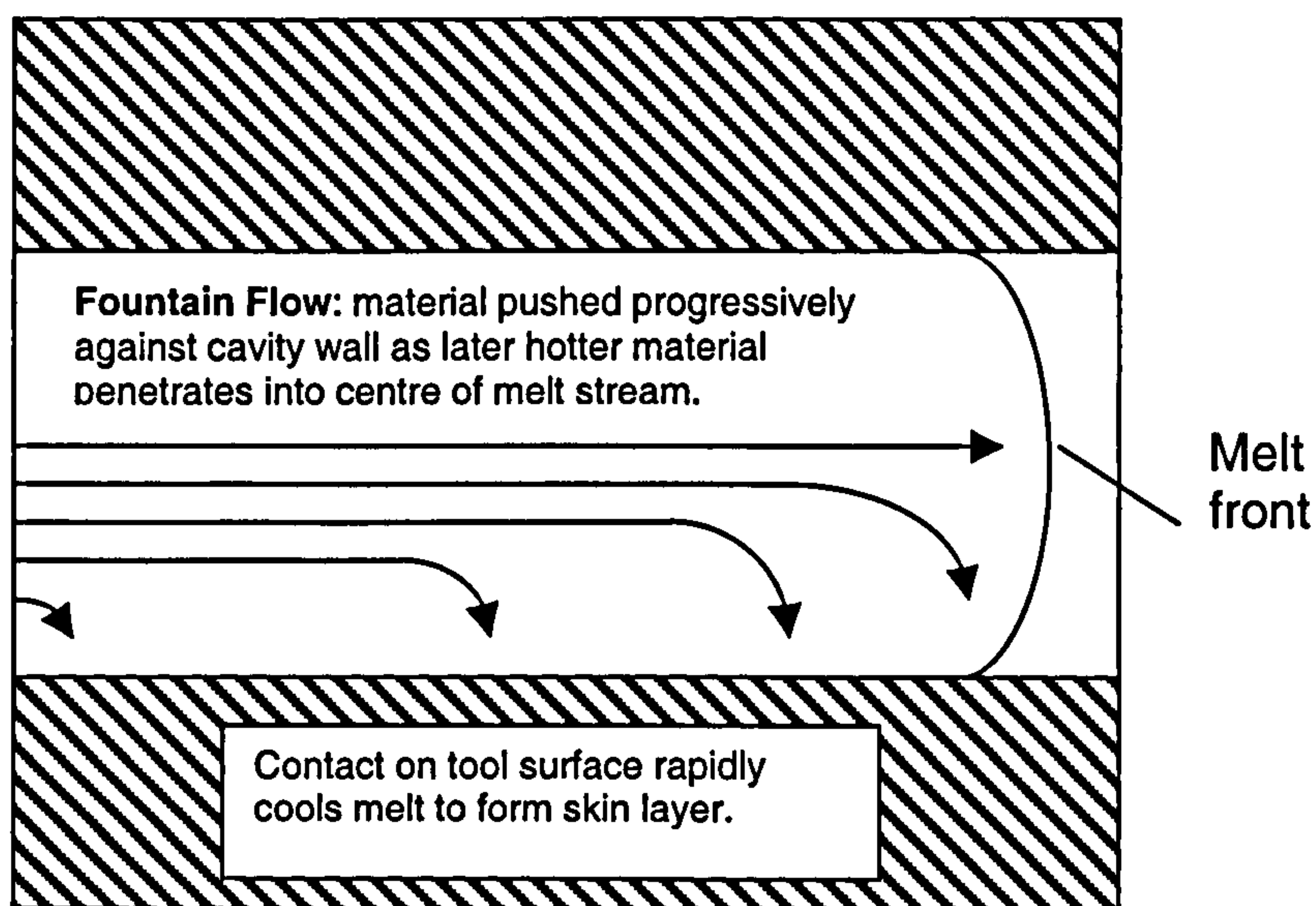


Figure 2-1 Schematic of Fountain Flow

As the mould has filled, a skin of solid plastic has formed on the wall. This causes a reduction in the effective gap, through which later molten material passes and so increases the shear rate. The extra shear stress causes

orientation of the molecular structure and the melt is generally too viscous to allow for relaxation of all the stress that is developed. The result is that the shrinkage of the material becomes much greater in the direction of flow and orientation that is in the radial direction, compared with that at right angles to it, the circumferential direction. Controlling the temperature of the mould can help to even out these effects [Wilkinson, 1999].

Of the moulding stages discussed, the parameters of mould filling, packing and cooling have been shown to be more important to final part quality than the plastication stage [Whelan, 1990].

2.1.2 Injection moulding structure

The result of the mould filling process can be seen in the injection mouldings of crystalline materials which typically exhibit a three layer microstructure due to the combined influence of flow, shear and temperature gradients [Woodward, 1995]. This is illustrated in Figure 2-2.

surface layer: also referred to as the skin, this section exhibits a high degree of frozen in orientation as it freezes quickly against the mould wall.

shear zone: present below the highly orientated layer, this exhibits regions of different morphologies.

core: this has a coarse crystalline structure, the core remains molten for longer and is more insulated from cooling effects.

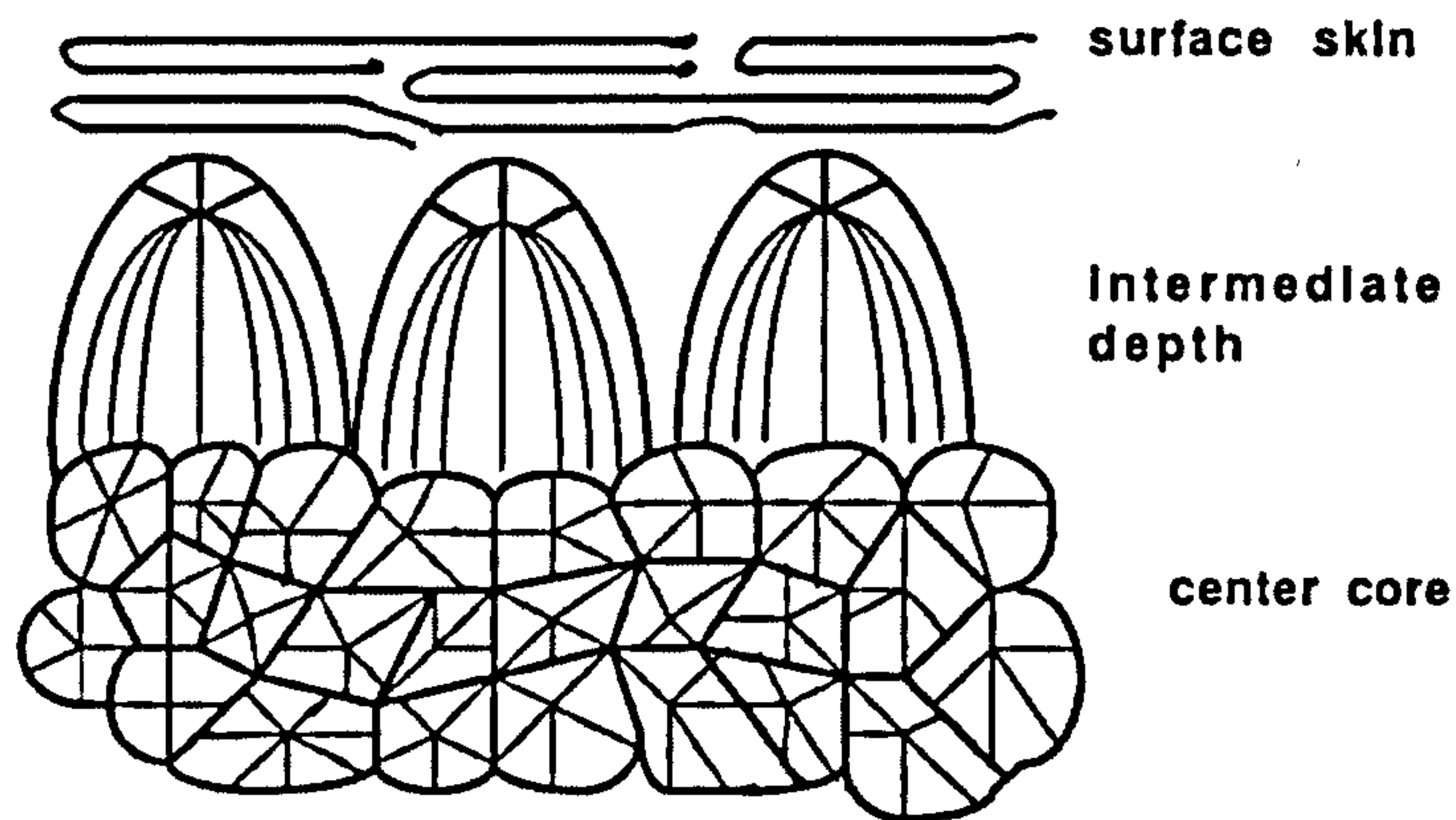


Figure 2-2 microstructure of crystalline injection moulding [Woodward, 1995]

The relative thickness of these microlayers depends on parameters such as mould temperatures, injection speeds and tool geometry. Thinner sections will generally require faster injection speeds than thick walled parts, mainly because of the decrease in the importance of the relationship between mould filling time and cooling time with a thicker section [Woodward, 1995].

A common practice is to use a profiled injection speed that begins slowly and then increases, as the end of the filling stage approaches it is decreased again [Whelan, 1990]. A three stage profile is usually adequate in most cases. This switch from mould packing to holding pressure is the most eventful as the material viscosity is drastically changed. It is vividly described by Wagner [Wagner, 1994] 'as changing from flowing like honey to flowing like modelling clay'. This explains why consistently switching at the same point can make the difference between producing consistent parts by being in control of the process as opposed to producing rejects.

Variations on the basic injection moulding method have been developed. One of the most useful of these methods is co-injection moulding, also

known as sandwich moulding or 2K (two-component) moulding. A literature survey on these methods has been produced by Selden [Selden, 1997].

2.2 *Co-injection Moulding*

In co-injection moulding two compatible melts are injected sequentially into the mould thus forming a layered structure. The melt injected first forms the skin, whilst the melt injected afterwards forms the core. Using two polymers with different properties makes it possible to obtain unique property combinations that are not possible in ordinary injection moulding. Examples of these were given in Table 1-1.

The process was first described and developed by ICI in 1970 [Oxley, 1971] and was developed as an alternative to the structural foam process. By using a solid skin with a cellular core, it is possible to obtain a surface finish as good as for a solid part but with the added rigidity of the foam core. There is also the reduction in material cost associated with foaming. This requires less raw materials and is therefore cheaper to produce. In products with thickness above 4mm, this method is often used [Stephenson, 1996].

Different material combinations offer a number of options, a number of these including commercial illustrations were given in Chapter One.

2.2.1 Co-injection Moulding : Different Techniques

There are a number of variations of the co-injection moulding process which have been developed. They can be split into two types, sequential injection and simultaneous injection. This research uses the simultaneous method that has a number of advantages over the sequential method. The advantages and disadvantages of both these methods will now be introduced and discussed.

2.2.1.1. *Sequential Injection: Single Channel Technique*

The single channel method was patented by ICI in 1970 [Oxley, 1971]. An injection moulding machine with two cylinders is used and polymer melts are injected sequentially into a mould. A specifically designed valve is used, which allows injection of skin material, the flow is then stopped and the core injected. However this method has limitations, at the switch point there is a pressure drop. This switching of polymer flows can cause the flow to stop, giving surface defects such as shadow marks or gloss marks on the mouldings [Selden, 1997]. As with all co-injection mouldings changing injection moulding parameters or the relative material viscosity can vary the skin/core structure, however it can be difficult to get even distribution of the core material. The process is mainly used for thick sectional parts with foamed cores [Whelan, 1989].

2.2.1.2. Sequential Injection: Mono Sandwich Technique

The mono sandwich technique was developed by Ferromatik Milakron. It uses two materials layered in a standard cylinder [Ferromatik, 1996] and is shown in Figure 2-3. They are then injected one after the other into the cavity. This is achieved by melting the skin material in a separate side extruder that plasticizes the material and leads it through a special hot runner to the front of the screw in the main cylinder. The melt pressure pushes the screw backwards. When a sufficient amount of melted material has accumulated in front of the screw, the screw starts rotating and feeds the core material. The injection is then done in the same way as for normal injection moulding by pushing the screw forward.

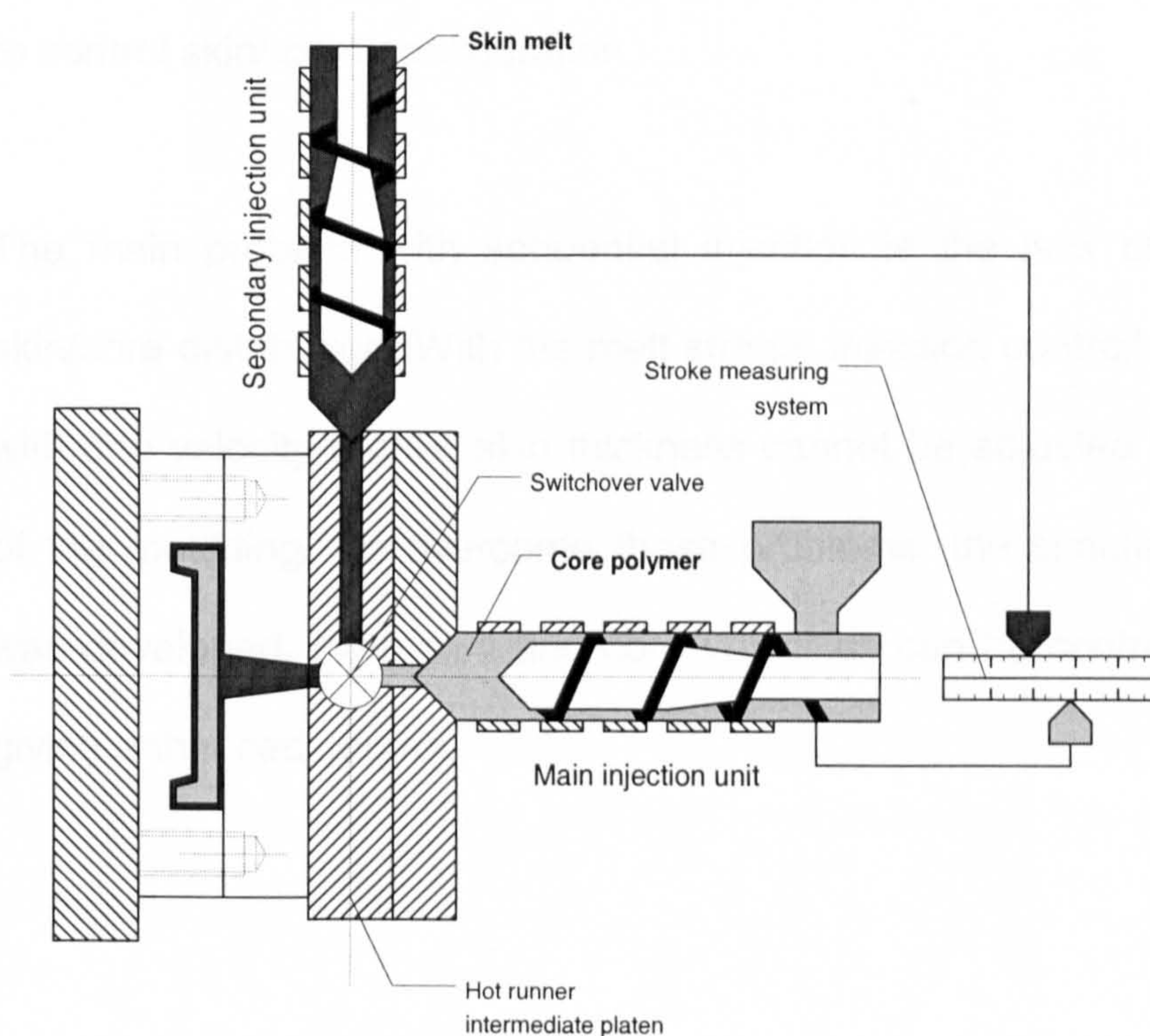


Figure 2-3 Ferromatik Mono Sandwich technique [Ferromatik, 1996]

The maximum amount of core material that can be obtained depends on the mould geometry. For simple symmetrical parts this value is 65-75% by volume [Selden, 1997], which is somewhat higher than for the two channel technique which will be discussed later. A standard moulding machine can be rebuilt to a sandwich machine simply by connecting a side extruder to the main injection unit. Also, very thin-walled parts can be produced by the method. A further advantage is the speed of colour and material change compared to other sandwich techniques due to the relatively simple construction [Ferromatik, 1996]. The process control is simple since injection is made in the same way as for normal injection moulding. The drawback to this method is that by feeding through one injection unit, there is a lack of detailed control that is required when moulding complex shapes to control skin/ core configuration.

The main problem with sequential injection is the lack of control in the skin/core distribution. With the melt stream injection controlled together and with one velocity profile, skin thickness cannot be adjusted in various parts of the moulding. To overcome these problems, the simultaneous method was developed. Here skin and core velocities can be controlled separately giving enhanced control.

2.2.1.3. Simultaneous Injection: Two Channel Technique

The two channel method, developed by Battenfeld in the mid-1970s, includes a phase of simultaneous injection [Eckhart, 1987]. Two injection units are joined through a specially designed nozzle. In the Battenfeld design shown in Figure 2-4, the nozzle is equipped with two separate concentric channels that can be independently, operated, opened, and closed hydraulically [Eckhart, 1987].

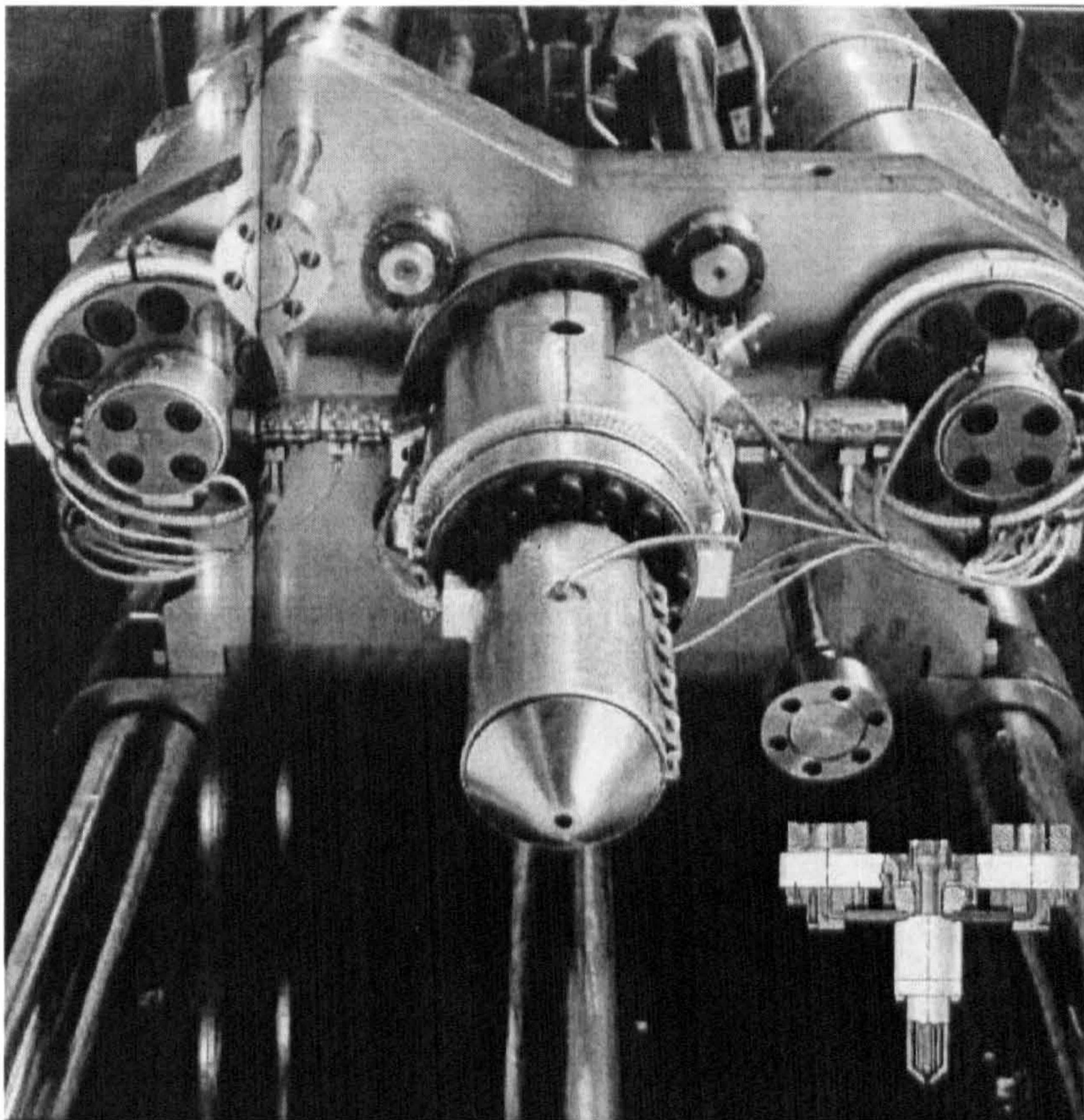


Figure 2-4 The two nozzle channel on a Battenfeld co-injection machine [Eckhart, 1987]

A phase of simultaneous injection of skin and core avoids the problems

inherent in the single channel technique by maintaining a constant flow front velocity. This can be seen by looking at Figure 2-5 and comparing the pressure profiles and screw velocity of the simultaneous and single channel methods. In the sequential method, the period of stagnation after injection of A before injection of B can be clearly seen, resulting in a drop of cavity pressure and a period where there is no movement of material in the screw. This demonstrates many of the limitations of sequential injection discussed in section 2.2.1.1.

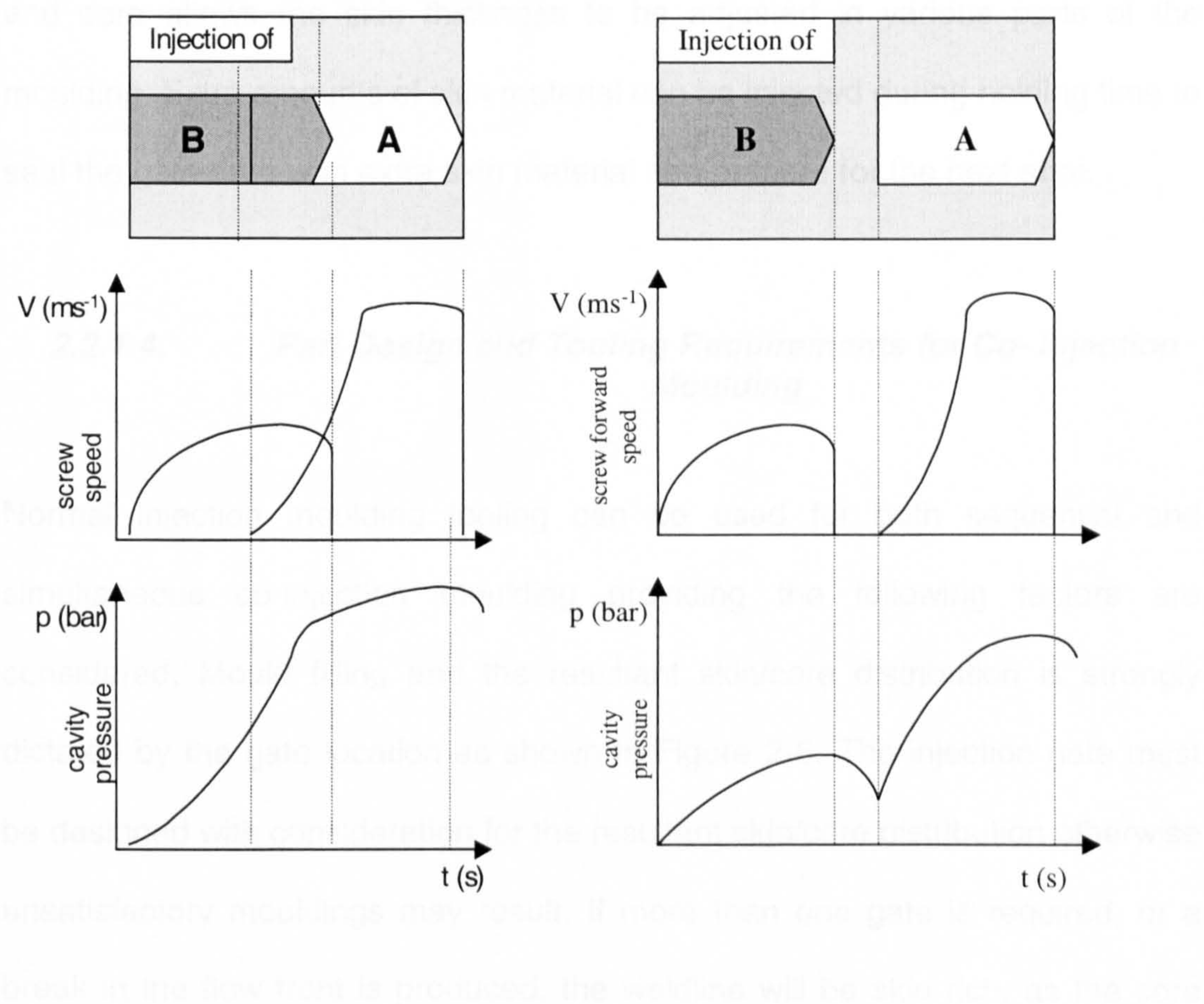


Figure 2-5 Comparison of mould filling of simultaneous (left) and sequential (right) injection moulding

[Battenfeld operating manual for co- injection moulding machine BMT-1100]

The length of the simultaneous injection phase depends on the material and especially on the mold geometry. Typically the duration is 25 % of the injection time for the skin component [Selden, 1997]. Separate operation of two injection units makes it easier to control skin thickness in various parts of a moulding. Mould filling dynamics dictate optimum distribution of core material is obtained if the skin viscosity is kept slightly lower than that of the core [Somnuk,1995]. This is due to rheological factors that will be explained in more detail in Chapter Three. The ability to separately control the velocity profile of the skin and core allows the skin thickness to be adjusted in various parts of the moulding. Extra amounts of skin material can be injected during holding time to seal the gate area with extra skin material and prepare for the next shot.

2.2.1.4. *Part Design and Tooling Requirements for Co- injection Moulding*

Normal injection moulding tooling can be used for both sequential and simultaneous co-injection moulding providing the following factors are considered. Mould filling and the resultant skin/core distribution is strongly dictated by the gate location as shown in Figure 2-6. The injection gate must be designed with consideration for the resultant skin/core distribution otherwise unsatisfactory mouldings may result. If more than one gate is required, or a break in the flow front is produced, the weldline will be skin rich, as the core materials will not completely meet due to the filling dynamics of co-injection moulding. The skin will always pack these areas before the core material can reach them. This is illustrated in Figure 2-6.

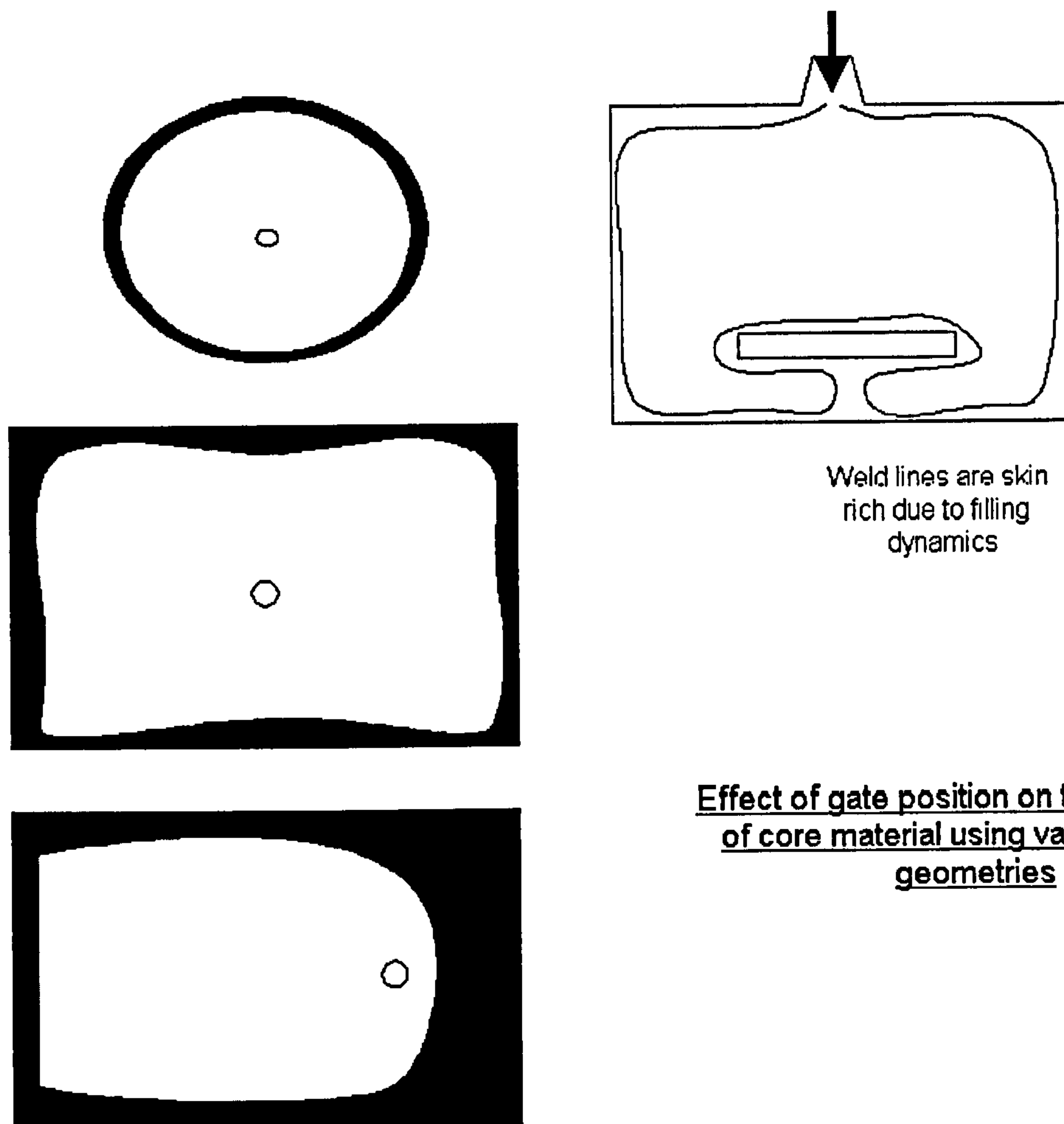


Figure 2-6 Gate position effects

2.2.1.5. Three Channel Technique

Again, due to the dynamics of mould filling, material entering the tool and cooling on the walls near the gate can get remelted and flushed away due to frictional heat generated by the incoming molten flowing melt. This can lead to variations of skin thickness and leave the skin near to the gate region much thinner than on the rest of the moulding. This effect is generally more

pronounced on the opposite side of the gate due to the higher shear experienced in this region. In order to overcome this the three channel technique was proposed [Wood, 1991].

With the three channel technique, an extra channel is used for the skin in the centre of the gate in order to retain skin thickness in this area. An example of a system developed commercially by Kortec is shown in Figure 2-6. The extra channel can reach the opposite side of the moulding, enabling the two surfaces to be regulated separately and surface thickness controlled [Selden, 1997]. This special design can only be used with a central gate, otherwise skin/core distribution will be irregular as detailed in 2.2.1.4. For other gate geometries or multi-cavity mouldings, the two channel or single channel technique is preferred.

KORTEC THREE-LAYER NOZZLE FLOW

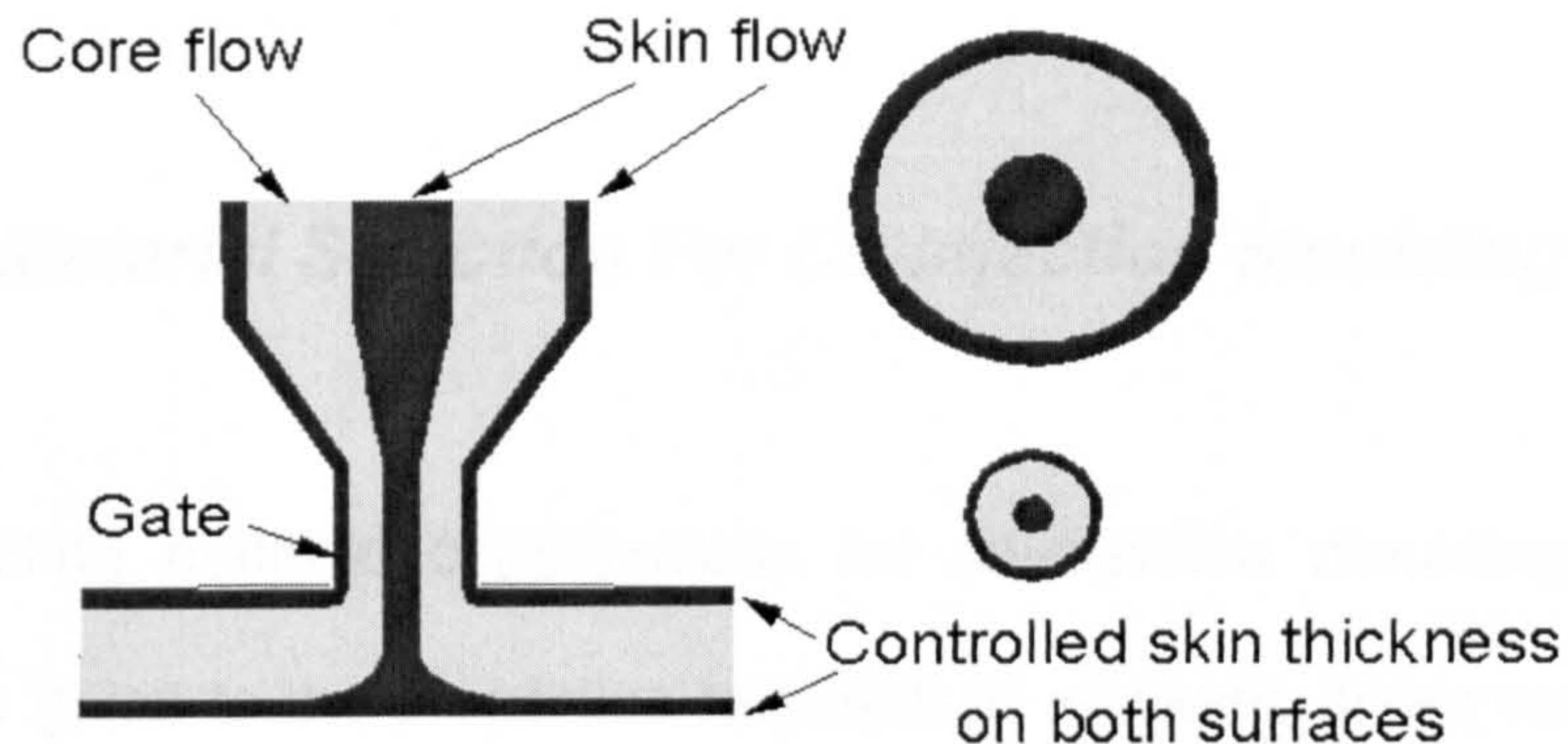


Figure 2-7 Three-channel nozzle technique [Kortec, 2001]

2.2.1.6. Gas-assisted

Gas assisted injection moulding is another variation of a co-injection system. Whilst gas assisted injection moulding is usually dealt with separately to co-injection moulding there are several technical aspects of this process specifically related to development of this research in multimaterial mouldings. For this reason, a brief description is included here.

In gas assisted injection moulding, a hollow core is produced by injecting an inert gas such as nitrogen into the polymer melt stream. It is analogous with co-injection moulding as the gas can be thought of as acting as the core material. The injected gas maintains pressure throughout the cycle, forcing the cooling skin against the mould walls. The injected gas follows the path of least

resistance, making channels in the hottest, thickest and least viscous parts of the melt stream [Stephenson, 1996]. This enables parts to be produced with thick and thin sections without sink marks or warpage [Belofsky, 1995]. The rest of this thesis will however concentrate on two polymer co-injection.

2.3 *Material Selection For Co-injection Moulding*

In selecting material combinations for co-injection moulding, consideration must be given to the properties required. In all cases, there must be a certain level of adhesion between skin and core. [Stephenson, 1996]

To achieve this, the two materials should:

- 1) Have approximately the same shrinkage and thermal expansion values.
- 2) Exhibit some degree of bonding at the interface.

Differences in mould shrinkage and thermal expansion could give sink marks, warpage and residual stresses [Selden,1997]. All result in a reduced quality component. Interfacial bond strength is required to maintain mechanical integrity through global load sharing, otherwise the properties will come from a significantly reduced section thickness, that of the skin alone. For good adhesion, a certain amount of interdiffusion is required between the melts. This can be achieved when there is a high compatibility, or solubility between the melts [Utracki, 1989].

Tables of compatible and incompatible material combinations are available, such as shown in Table 2-1. However caution is required when using such tables, since it has been shown that the exact grade of a certain material will affect the bond strength [Stephenson, 1996]. An optimum material combination

might therefore require a certain amount of trial and error. Through the addition of compatibilizers it is possible to chemically bond non-adherent materials [Utracki, 1989],[Brandrup, 1996]. These substances usually contain a third polymer that bonds to, or is soluble in, the two materials [Datta, 1996].

	ABS	ASA	EVA	PA6	PA66	PBT	PC	PE-HD	PE-LD	PET	PMMA	POM	PP	PPO mod	PS-GP	PS-HI	SAN	TPU
ABS	+	+	+			+	+	-	-	+	+	-	-	-	*	*	+	+
ASA	+	+	+			+	+	-	-	+	+	-	-	-	*	-	+	+
EVA	+	+	+					+	+				+		+	+	+	
PA6				+	+	*	*	*	*			-	*	-	-	-	+	+
PA66				+	+	*	*	*	*			-	-	-	-	-	+	+
PBT	+	+		*	*	+	+	-	-	+	-	-	-	-	-	-	+	+
PC	+	+		*	*	+	+	-	-	+		-	-	-	-	-	+	+
PE-HD	-	-	+	*	*	-	-	+	+	-	*	*	-	-	-	-	-	-
PE-LD	-	-	+	*	*	-	-	+	+	-	*	*	+	-	*	-	-	-
PET	+	+				+	+	-	-	+	-	-		-	-	-		+
PMMA	+	+				-		*	*	-	+		*	-	-	-	+	
POM	-	-		-	-	-	-	*	*	-		+	-	-	-	-	-	
PP	-	-	+	*	-	-	-	-	+		*	-	+	-	-	-	-	-
PPO mod	-	-		-	-	-	-	-	-	-	-	-	-	+	+	+	*	-
PS-GP	*	*	+	-	-	-	-	-	*	-	-	-	-	+	+	+	-	-
PS-HI	*	-	+	-	-	-	-	-	-	-	-	-	-	+	+	+	-	-
SAN	+	+	+	+	+	+	+	-	-		+	-	-	*	-	-	+	+
TPU	+	+		+	+	+	+	-	-	+			-	-	-	-	+	+

(-) : No adhesion, (*) : Poor adhesion, (+) : Good adhesion

Table 2-1 Material Compatibility Table [Rungseesantivanon, 2000]

Similar moulding temperatures for both materials are also recommended, since they are processed simultaneously [Eckhart, 1987]. The skin should have the same or preferably lower viscosity than the core. If the skin viscosity is too high, the core melt will break through the skin and form the surface layer. Adjustments to injection temperatures or other machine parameters such as an injection delay can be used to control the relative material distributions [Selden, 1997].

2.4 Previous Research in Co-injection Moulding

There is not a great deal of literature relating to the co-injection moulding of two polymers. Both commercial and research interest has been more focused upon similar processes such as gas assisted injection moulding. The research that has been published has tended to be concentrated on the mechanisms of skin/core distribution that are covered in Chapter Three. In relation to this research project, only six previous studies are relevant to multi-material moulding with one being by the author. A summary of these is given in Table 2-2.

Both Selden [Selden, 1998] and Rungseesantivanon [Rungseesantivanon, 2000] studied adhesion characteristics of the nylon/ polypropylene system with a maleic anhydride compatibiliser. Whilst neither specifically researched instabilities or reported surface defects in their systems, Selden does report the appearance of viscous fingering in his mouldings, which seemed to increase with increasing compatibiliser levels. This is similar to the viscous fingering commonly seen in gas assisted injection moulding (see section 2.2.1.6.). He attributes this effect to polymer instabilities based on the findings of Akay [Akay, 1983] who found similar instabilities in plates of an unfilled polypropylene skin with a talc filled polypropylene core. This is interesting, since this is a single polymer system and suggests instabilities may not be confined to immiscible systems. Analysis of cross-sectioned mouldings from both these researchers identified microlayers of skin/core mixing. Selden noted a stronger effect away from the gate area and that near the gate the effect

disappeared. However, neither investigated this phenomenon further and neither reported any surface defects.

It is feasible that ridges were found on mouldings by both these researchers but were not reported as they were not of interest to the authors. For example when duplicating the work of Rungseesantivanon in Chapter Seven, ridges were present on the mouldings. These mouldings used the same materials, machine and moulding parameters as those detailed by the researcher. It is therefore highly likely that other researchers have also overlooked the appearance of surface defects in their samples. Since these are mainly academic studies, the surface appearance of the samples are not likely to be of major importance. However, for commercial application of such research, surface appearance would be of more pressing concern.

In terms of the interface, Rungseesantivanon reported the main factor in adhesion strength was the thickness of the skin layer. This was due to the increased bonding time available for adhesion with a thicker and therefore slower cooling interface. A thinner layer would also be subject to higher shear from incoming molten material and be more likely to be remelted and swept away into the melt stream. This would tie up with the earlier claim of Selden that the microlayers disappeared towards the gate area as this would be the area subject to remelting from shear effects from incoming material.

Eigl and Langbecker [Eigl, 1998], attempted to model the layer thickness formation and melt flow instabilities in co-injection moulding. They split instabilities into two types.

- A) Viscous fingering, caused by viscosity differences in the melt streams and
- B) Interfacial Instabilities caused by local layered structures at the boundary layer of skin and core described as 'laminates'. These would correspond to the microlayers reported by Akay and Selden.

They claimed both of these phenomena occurred individually and were not related to each other. Again no mention was made of any surface defects.

Kadota et al [Kadota, 1999] studied a polypropylene (PP)/ Polystyrene (PS) system. They found skin thickness to vary across the moulding and claimed this indicated an unstable system. They also found that injection speed was the key parameter in getting uniform skin distribution. Lower speeds were most effective. Injection speeds were also found to be of major importance in the work of Goodship and Kirwan [Goodship, 2001, a]. They studied both compatible and incompatible systems. They found in compatible systems of acrylic and polycarbonate that increased core speed could produce turbulence in the gate region of the moulding. They also studied an incompatible system of PS and High Density Polyethylene (HDPE). In this case, higher injection speeds produced wave like structures at the interface. The authors also report surface defects in compatibilised PA12/ PP structures such as the 'halo' defect as shown in Fig 2-8, attributed to stress differences at the interface.

Whilst these studies shed some light on possible material interactions, there are numerous areas in the literature where research is lacking, for example, data relating co-injection mouldings to standard injection moulding. How does the effect of injecting a second material affect the microstructure shown in

Figure 2-2? and what happens if these systems are immiscible ? An understanding of the material and process inter-relationships and the mechanisms at work during formation of the skin/ core interface is required in order to fully understand why a defect such as a ridge can occur. Therefore, much of the work in this research project is fundamental and novel.

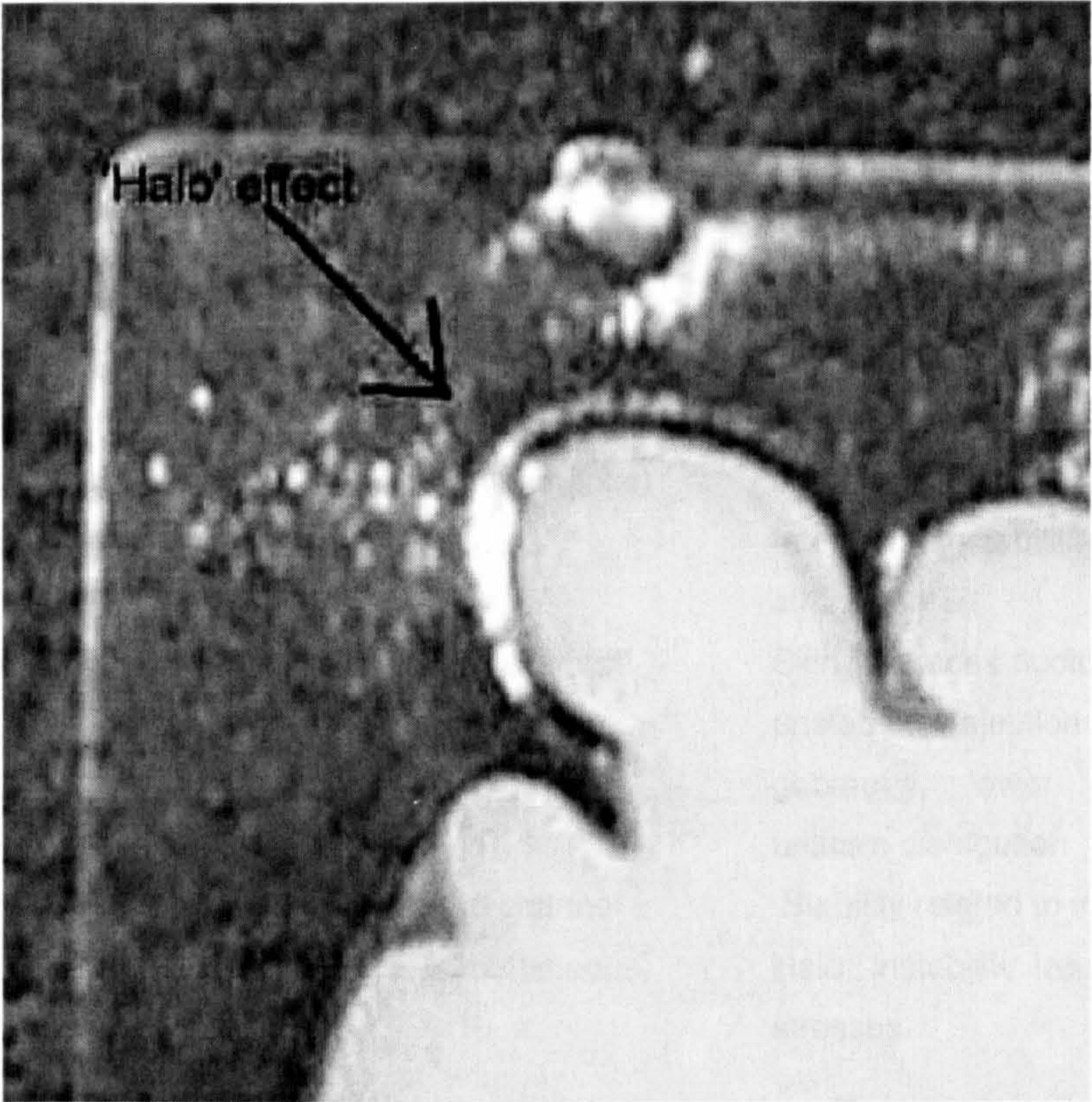


Figure 2-8 'Halo' defect in PA12/PP mouldings

2.5 Discussion and conclusions

Co-injection moulding provides processing routes for obtaining polymer combinations that are in general, not possible with conventional injection moulding.

Workers	Co-injection techniques	Claims
Akay [1983]	Two channel (simultaneous)	Non-symmetrical flow effects. Instability if high viscosity skin and high loading speeds.
Selden [1998]	Two channel (simultaneous)	Development of mixed layer. Increased with injection speed and increased skin viscosity. Disappeared near gate.
Rungseesantivanon [2000]	Two channel (simultaneous)	Simultaneous injection time has non-linear correlation to skin/core viscosity ratios Skin layer was not a uniform thickness being thinnest at gate area.
Eigl and Langbecker [1998]	Two channel (simultaneous)	Viscous fingering caused by viscosity differences Interfacial Instabilities caused by local layer structures
Kadota et al [1999]	Two channel (sequential)	Skin thickness fluctuates, indicating system unstable. Injection speed effects core geometry, lower speeds giving more uniform distribution
Goodship and Kirwan [2001]	Two channel (simultaneous)	Stability related to injection speeds Halo instability as a result of built up stresses.

Table 2-2 Co-injection moulding research with Incompatible polymers

2.5 Discussion and conclusions

Co-injection moulding provides processing routes for obtaining property combinations that are, in general, not possible with conventional injection moulding.

However, there are a number of factors that have limited the commercial use of co- injection moulding technologies.

- High capital cost. Co-injection machines are around 40% more expensive than an ordinary injection moulding machine [Selden, 1997].
- Restrictions with regard to mould geometry: parts with sharp corners, changes in wall thickness, ribs or bosses are difficult with co-injection moulding due to the problems of distributing skin and core materials [Eckhart, 1987].
- Weld lines; at weld lines there is only skin material, and special solutions, like overflow channels, are necessary if the core material is needed here.
- There is a complicated and poorly understood relationship between rheology and process parameters. Inter relationships exist between melt temperature, viscosity, and temperature differences between the skin and core melts.
- Restrictions with regard to material combinations. Even for compatible materials, the choice of a certain grade could influence adhesion and give inferior properties. Since processing conditions can affect the rates of inter-diffusion of skin and core, it can also affect the properties of the final component. Again, the effects are complicated and not well understood.

This research specifically addresses the final two of those limitations. The interactions that take place during co-injection moulding are not well researched and with this in mind, the following chapters will look at the rheological and thermodynamic interactions taking place.

Chapter 3. Physical Properties of Polymer Melts

To understand and evaluate the processing behaviour of materials during co-injection moulding, it is necessary to have knowledge of both the rheological and thermodynamic properties of the materials in question. How a material responds to changes in temperature, shear and pressure can greatly affect processing methods and strategies. Other material properties such as density, elasticity, thermal expansion and thermal conductivity can also affect processing behaviour through for example decisions on the cooling rates required, shrinkage tolerances and die swell.

The following sections will introduce these properties and then relate them with regard to the co-injection moulding process.

3.1 *Thermal Diffusivity*

Compared to materials such as metals, polymers have very low values for thermal diffusivity of about $10^{-7} \text{m}^2/\text{s}$ [Agassant, 1991]. To overcome this, processing methods have developed which rely on plasticating relatively thin layers of polymer such as seen in the use of extrusion screws. In this way, long residence times and low flow rates can be avoided. Once the polymer is plasticated then it is the flow properties that become of primary importance to the success of a processing operation.

3.2 Rheology

In seeking to study co-injection moulding and its effects on the polymer materials being used as skin and core components, it is important to have a better understanding of what is, in effect, stratified flow of viscoelastic fluid. This can be done through the study of rheology.

Rheology deals with deformation and flow and examines the relationship between stress, strain and viscosity. Most rheological measurements measure quantities related to simple shear such as shear viscosity and primary and secondary normal stress differences [Cogswell, 1996]. Material melt flows can be split into three categories, each behaving differently under the influence of shear as shown in Figure 3-1: Dilatent (shear thickening), Newtonian, Non-Newtonian pseudoplastic (shear thinning).

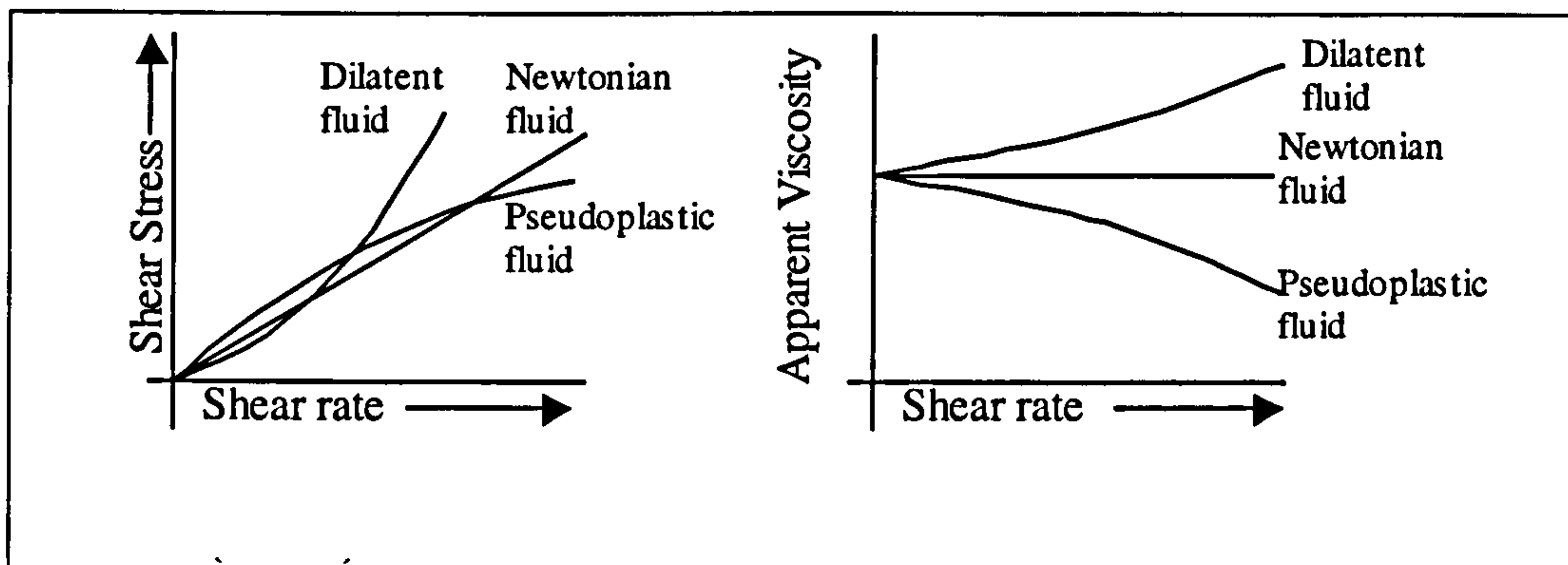


Figure 3-1 Typical stress/shear relationships (left) and apparent viscosity/shear curves (right) [Brydson, 1999]

In an ideal Newtonian liquid flow, the viscosity is independent of shear rate. Plastics fall into the category exhibiting shear thinning behaviour. They

respond to increased shear by a drop in viscosity. It can be seen from Figure 3-1 however that all melts approximate to Newtonian fluids at very low shear rates.

3.2.1 Simple Shear

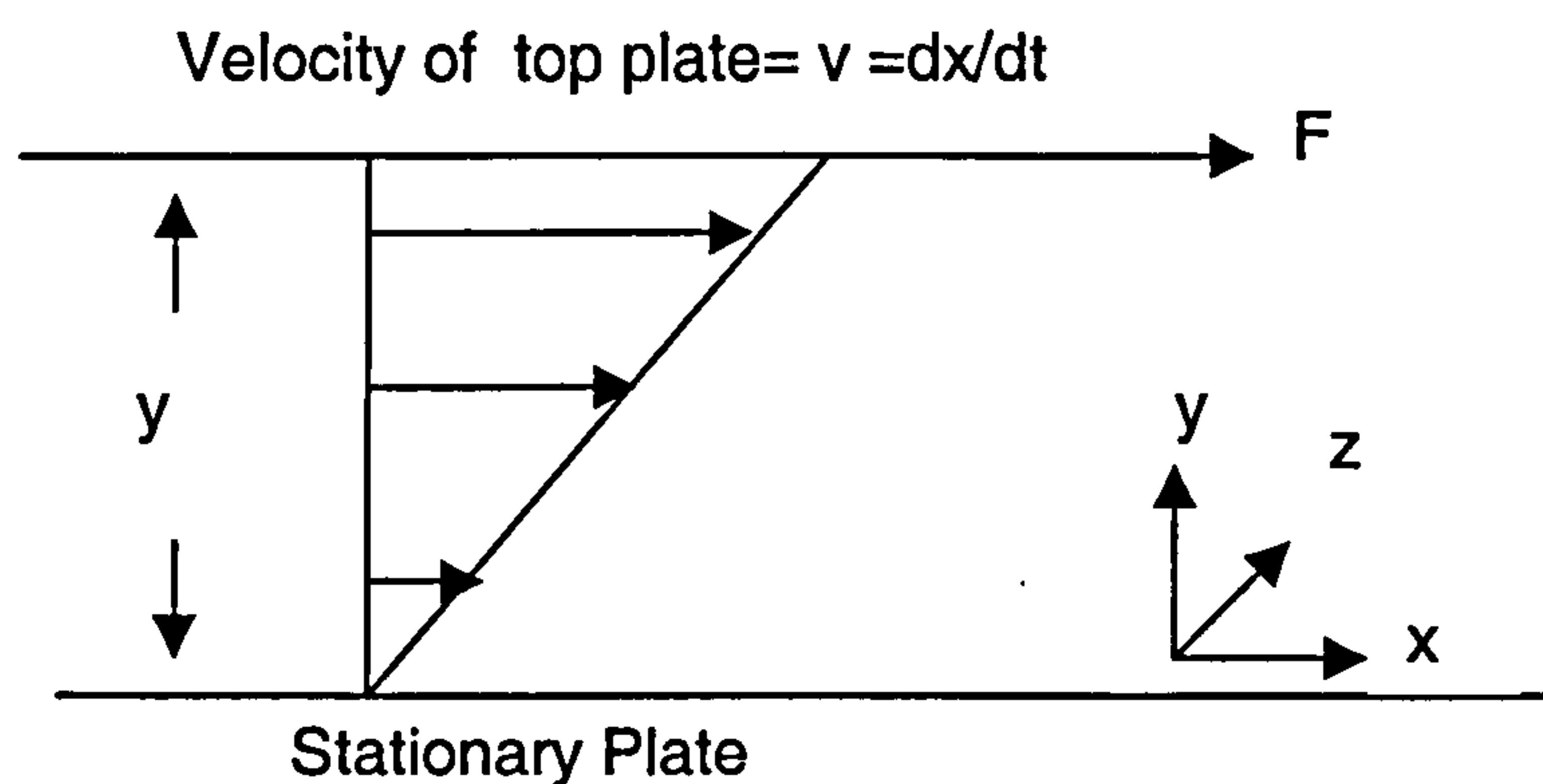


Figure 3-2 Simple shear deformation

In processing there are two major classes of simple shearing flows. Simple Shear is modeled by a Newtonian liquid moving between two parallel plates (shown in Figure 3-2), one which is stationary and the other applying a force F on the melt. A linear velocity gradient occurs between the stationary melt and the melt moving with the same velocity as the moving plate. The gradient is known as the Shear Rate which should remain constant.

The formula for Newtonian viscosity is:

$$\eta = \frac{\tau}{\dot{\gamma}}$$

Equation 1

where τ is shear stress, $\dot{\gamma}$ is shear rate, and η is viscosity.

This relationship between shear stress and shear rate is called the flow law or rheological equation of state [Michaeli, 1995]. This formula only applies to flow along a channel of uniform cross-section, as it is subjected to shear stresses only.

The type of flow representative of the injection moulding process is known as Poiseuille flow, which is shown in Figure 3.3. In this case both plates are stationary, and the flow is driven by a pressure gradient. As such, the velocity of the melt, assuming there is no slip, would be zero at the walls.

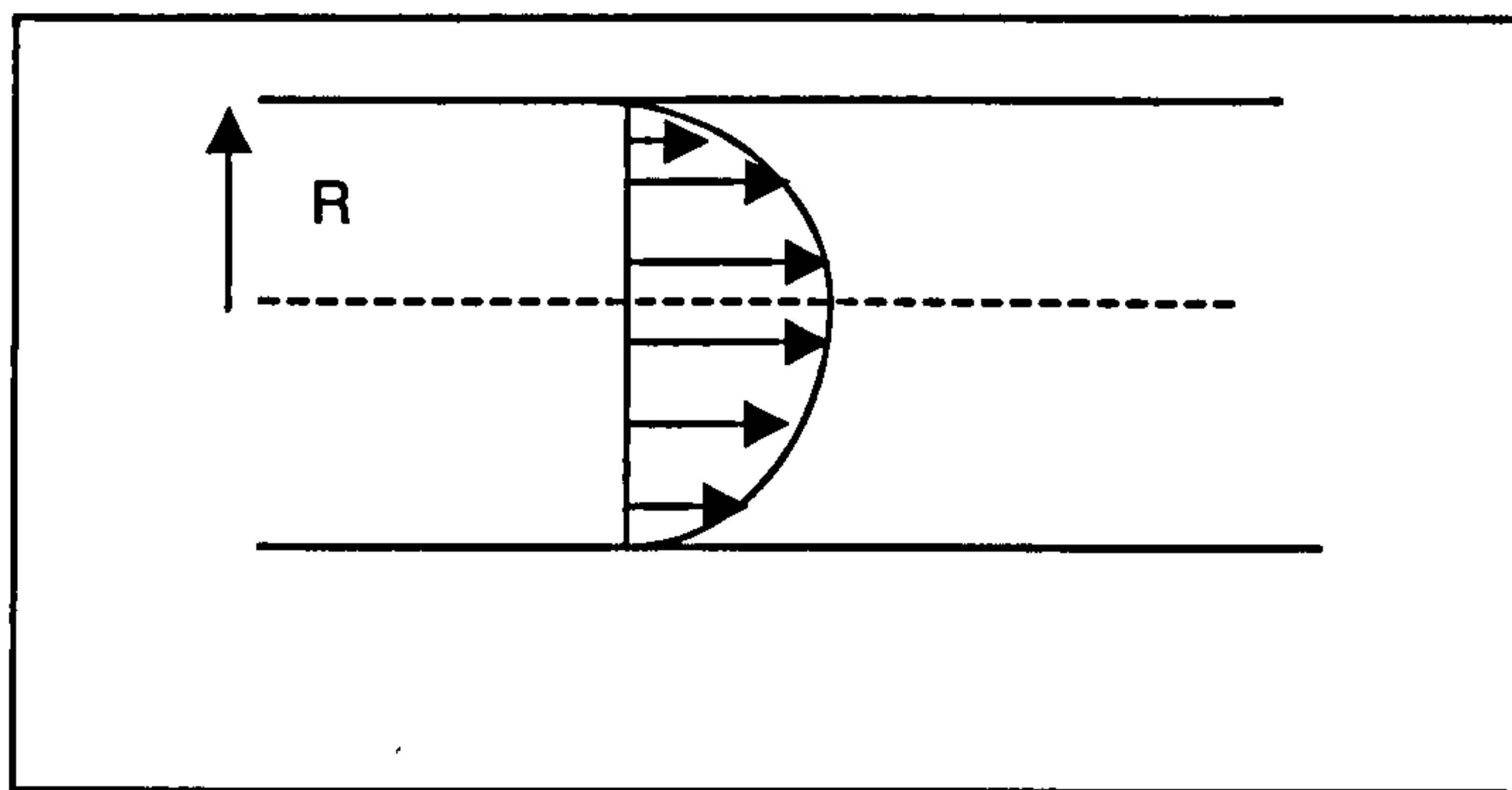


Figure 3-3 Poiseuille flow in a capillary [Brydson, 1999]

3.2.2 Shear rates associated with polymer processing

In a typical polymer processing operation viscoelastic fluids are forced to flow rapidly through complex and confining geometries under high stresses.

Shear rates for common polymer manufacturing processes are given below [Cogswell, 1996]

Compression moulding	$\dot{\gamma} = 1 \text{ to } 10 \text{ sec}^{-1}$
Calendering	$\dot{\gamma} = 10 \text{ to } 10^2 \text{ sec}^{-1}$

Extrusion	$\dot{\gamma}$ 10^2 to 10^3 sec^{-1}
Injection moulding	$\dot{\gamma}$ 10^3 to 10^4 sec^{-1}

Injection moulding is a high shear process with maximum shear rate usually occurring in the sprue. Rheological data relating to this process should therefore be representative of these rates.

3.2.3 Relating Shear Rate to the Moulding Process

Cogswell [Cogswell, 1996] provides a formula to closely approximate the maximum shear that will occur in the injection moulding process.

$$\dot{\gamma} = \frac{10}{D^3} \frac{M}{TN} \text{sec}^{-1}$$

Equation 2

Where: M is the part weight (g), D is the sprue diameter (cm), T is the injection time (s), and N is the number of injection ports. This formula allows calculations on the shear related to specific sprue geometries to be calculated.

3.2.4 Determination of Viscous Flow Behaviour

To measure the rheological properties of a polymer, the method that most approximates the conditions found in co-injection moulding is the capillary rheometer, a diagram of a single channel rheometer is shown in Figure 3-4. Other methods such as cone and plate rheometry are not able to attain the high shears associated with this processing method.

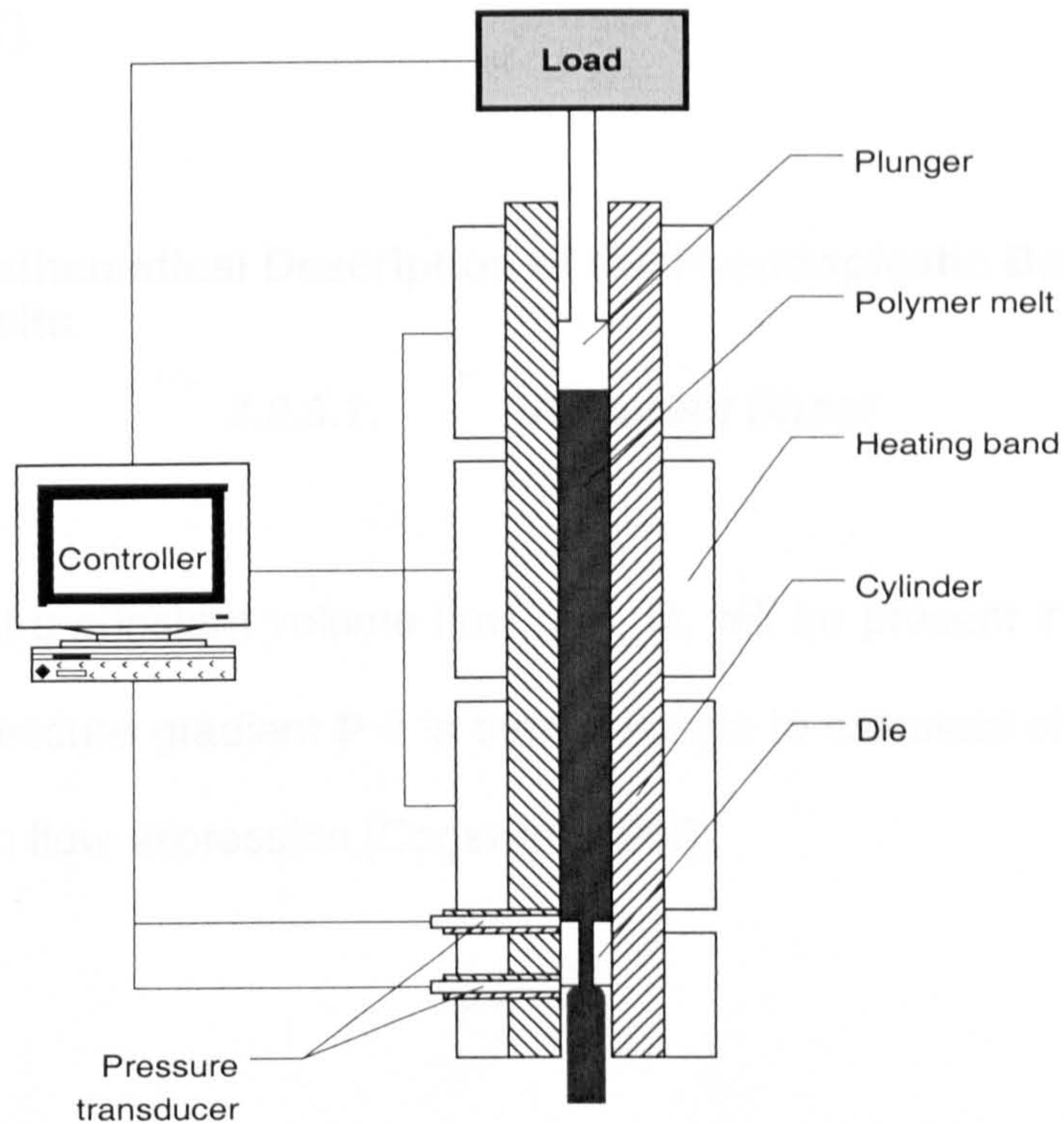


Figure 3-4 Capillary Rheometer

The principle of the measurement is by determining pressure loss in a capillary with an exactly defined geometry and known volumetric output rate at a constant melt temperature. Thus, shear can be calculated as the following, where P_L is the pressure at the full length die and P_o is the pressure at the zero length die:

$$\tau = \frac{(P_L - P_o)R}{2L}$$

Equation 3

where L is the length of the capillary and R the radius.

This method assumes both unidirectional and laminar flow with no wall slip [Carreau,1997].

3.2.5 Mathematical Description of the Pseudoplastic Behaviour of Melts

3.2.5.1. Apparent Shear

Assuming that a constant volume flow rate, **Q**, will be present in the Capillary due to the Pressure gradient **P** it is then possible to calculate shear rate from the Newtonian flow expression [Cogswell, 1996].

$$\dot{\gamma} = \frac{4Q}{\pi R^3}$$

Equation 4

where **R** is the radius of a channel with a uniform cross-section. Since polymers are not generally Newtonian the above is often referred to as the apparent shear rate. The shear stress, **τ** , can be calculated as:

$$\tau = \frac{PR}{2L}$$

Equation 5

where **L** is the length of the capillary.

The above formulas can be combined to form a definition of apparent viscosity as the ratio of shear stress to apparent shear rate:

$$\eta = \frac{\pi PR^4}{8LQ}$$

Equation 6

3.2.5.2. True shear

True shear takes into account the non-Newtonian behaviour of plastics to obtain the true viscosity curve. By multiplying apparent shear by a factor of $\left(\frac{3n+1}{4n}\right)$, the true shear rate for a non-Newtonian melt can be derived. This ratio is known as the Rabinowitsch Correction Factor. Thus true shear rate can be calculated as:

$$\dot{\gamma} = \left(\frac{3n+1}{4n}\right) \frac{4Q}{\pi R^3}$$

Equation 7

where the value n is dependent on the material and is usually between 1 and 0. However, since this factor does not affect the ratio of values, for comparative purposes it may be unnecessary to apply this correction.

3.2.5.3. Power Law

It has also been found that for the range of shear rates used in polymer processing, the non-Newtonian fluids' behaviour is dictated to by the Power Law .

The Power Law is:

$$\tau = \tau_0 \dot{\gamma}^n$$

Equation 8

where τ_0 and $\dot{\gamma}_0$ represent values of shear stress and shear rate in some arbitrarily chosen standard state, and $\dot{\gamma}_0$ has been nominated as 1. In the Newtonian case $n=1$, in shear thinning $n<1$, and the lower the value the greater the divergence from Newtonian behaviour.

3.3 *Factors affecting the viscosities of materials*

The following factors can affect the viscosity of materials :

- Temperature
- Pressure
- Molecular weight
- Formulation: fillers and additives

Molecular weight and formulation are specific to material grades. However, temperature and pressure vary both during the materials cycle from melting to cooling and because of the mould filling process where temperature and pressure gradients exist through the component. The effects of these properties and material properties on a typical viscosity curve are shown in Figure 3-5. These interactions will now be looked at more closely.

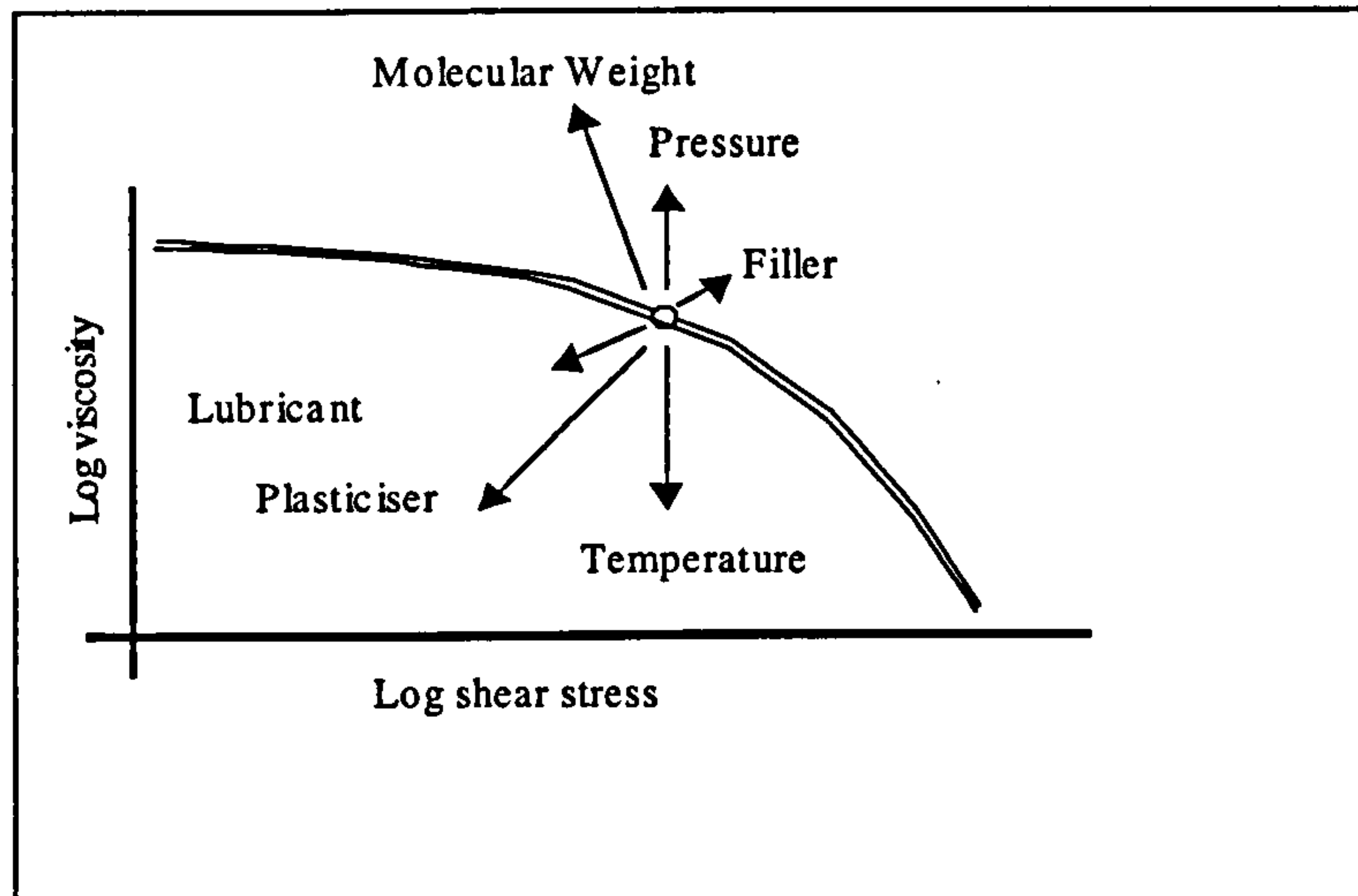


Figure 3-5 Effects of various factors on viscosity [Cogswell, 1996]

3.3.1.1. Temperature

The effect of temperature on the viscosity is more pronounced at low shear rates when compared to that at high shear rates. For one polymer melt, if the viscosities at different temperatures are presented in a log-log plot it can be seen that their shape remains the same while the location changes. This principle allows production of master curves by superimposing the lines along a slope of -1 . This effect is known as the temperature shift principle and can be seen for an unfilled polypropylene in Figure 3.6.

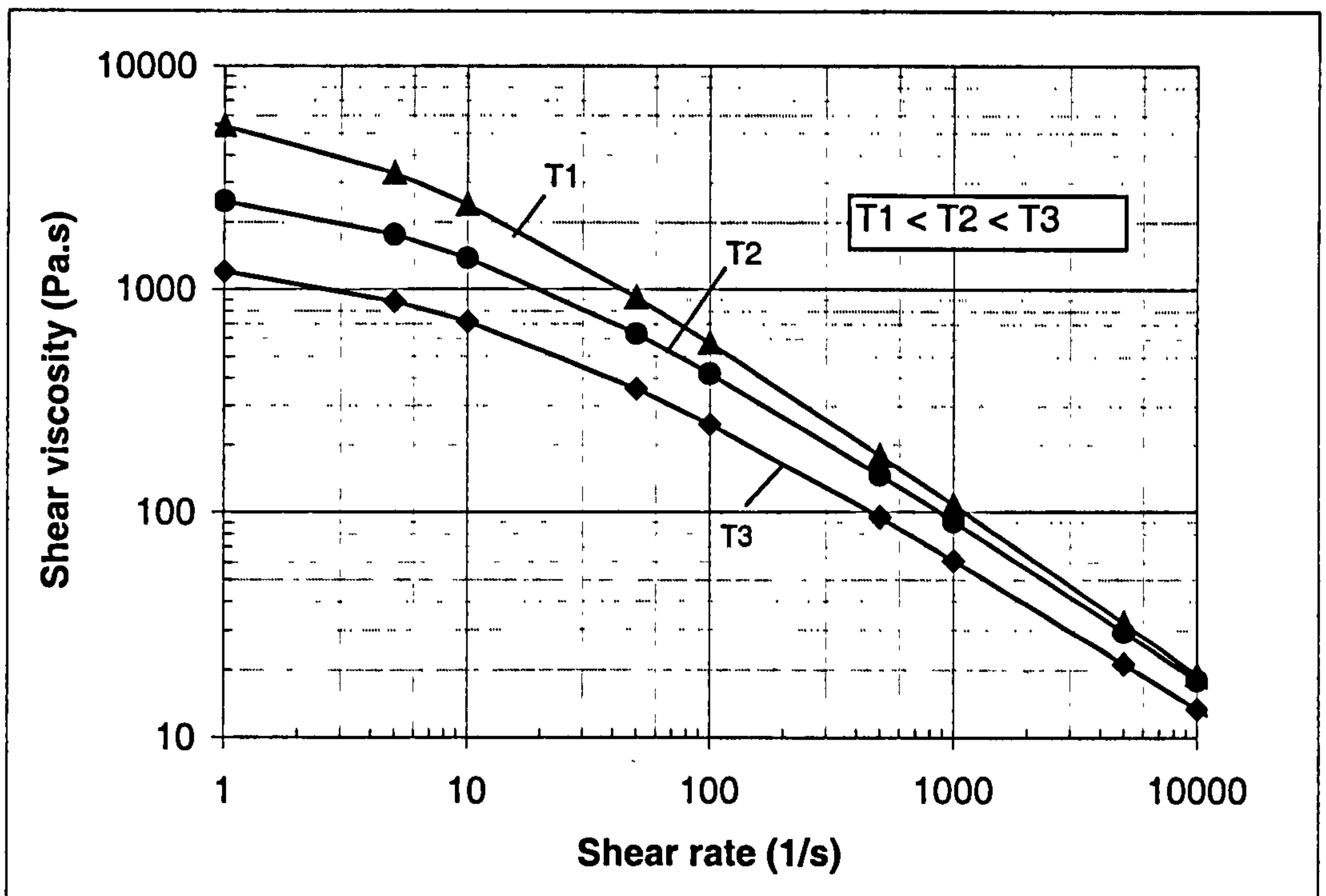


Figure 3-6 Polypropylene viscosity against shear rate for various temperatures

3.3.1.2. Pressure

Increasing pressure reduces both free volume and molecular mobility and leads to an increase in viscosity. In polymer processing the combined effects of high pressure and low temperature will tend to promote crystallisation. This can lead to situations whereby the material flows less as the pressure increases [Cogswell, 1996].

3.3.1.3. Molecular Weight

Most polymers are pseudoplastic, and their natural elasticity tends to allow orientation under shear [Berins, 1991]. At lower shear there is opportunity for the polymer chains to re-coil faster than they are being oriented, this will stop

the chains flowing so freely over each other. At higher shear, the greater orientation allows the chains to flow more freely.

Molecular weight is the single most important parameter in determining the viscosity of a polymer [Cogswell, 1996]. Where viscosity is normally proportional to molecular weight, proportionality is lost at a critical molecular weight value [Michaeli, 1992]. Polymers of lower molecular weight will have lower viscosities and be easier to process. Polymers of higher molecular weight will have superior strength properties but are more prone to be orientated during moulding and hence have poorer properties across the flow front. This is due to the longer chains requiring a greater time to relax into their original coil, hence showing more non-Newtonian behaviour at lower shear rates.

A variant on the effect of molecular weight is the molecular weight distribution. A narrow distribution will have chains with a similar amount of entanglement that results in uniform stressing, a broad distribution will have the longer chains tangle with each other and form a protective network around the shorter chains. Commercial polymers tend to have a large distribution of molecular weight [Agassant, 1991] with the viscosity a function of the average molecular weight and the distribution [Brydson, 1999].

3.3.1.4. Others

Fillers, including rubber modification, tend to increase the viscosity of melts, often resulting in super-imposable curves (identical but separated by some distance). Plasticisers and lubricants tend to decrease the viscosity of

polymers. This is due to their relatively low molecular weights, which impart added flexibility to the polymer system.

3.4 Impact of Rheology on the Dual Injection Process

The effect of viscosity on skin/core formation was described by Cogswell [Cogswell, 1996] and is shown in Figure 3-7.

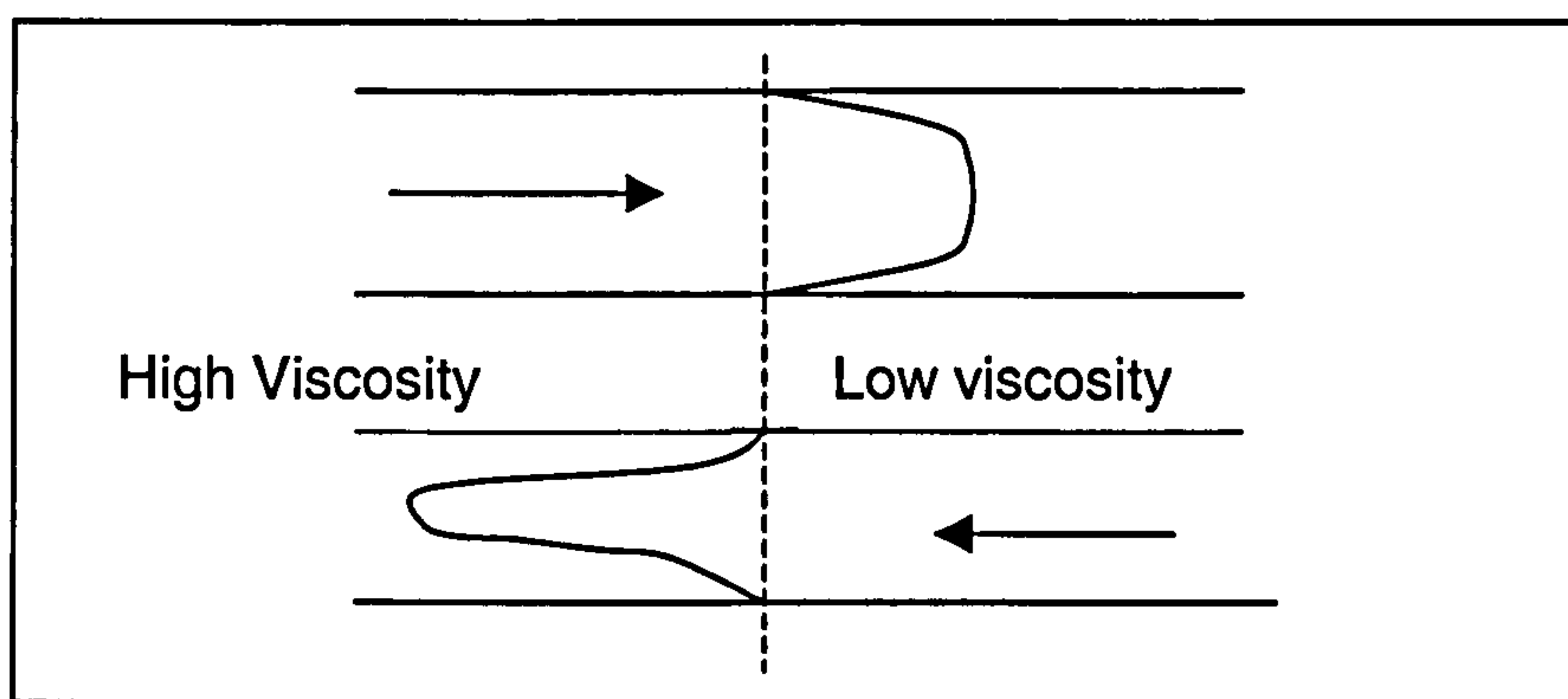


Figure 3-7 Interface behaviour of melts of different viscosity [Cogswell, 1996]

High viscosity melts flowing into low viscosity melts will force the low viscosity material in front of it. Low viscosity melts flowing into high viscosity melts will jet through areas of least resistance, giving a 'melt fingering' type effect. This type of effect can also be seen in gas assisted injection moulding where the core component, gas, has an effective viscosity of zero. The injected gas follows the path of least resistance, making channels in the hottest, thickest and least viscous parts of the melt stream [Stephenson, 1996]. Breakthrough of the core component in co-injection moulding can cause unwanted surface

defects, whereby the core material can be visible in the corners of the mouldings. Therefore, a high percentage of co-injection studies have investigated the relationship between the relative viscosities of the materials used within the process and the resultant skin/ core distribution to reinforce these findings.

3.4.1 Previous studies on the effects of viscosity ratios

White and Dee [White, 1974] found that two-phase flows are sensitive to differences in the rheological properties of the melt. Different rheological combinations produced different skin/core ratios. Later White and Lee [White, 1975] proposed a simultaneous system driven by viscosity encapsulation phenomena as shown in Figure 3-7. Young et al [Young, 1980] further developed this idea and found viscosity rather than normal stress to dominate skin/core distribution and interface shape. Somnuk and Smith [Somnuk, 1995] using PP as both skin and core found that for good skin/core distribution viscosity ratios must lie within a range 0.8-1.8 of each other.

Lee et al. [Lee, 1998] also found this to be the case. They also found the moulding parameters having most effect on the skin/core distribution were melt temperature, injection rate and the length of the simultaneous phase. In terms of other processing effects Cheng et al [Cheng, 1995] found there was considerable melt flow in the region of the gate during the post-filling process of co-injection moulding. These studies are summarized in Table 3-1.

Workers	Co-injection techniques	Claims
White and Dee [1974]	Single channel (sequential)	$\eta_{\text{skin}} \leq \eta_{\text{core}}$ produced good skin-core structure.
White and Lee [1975]	Single channel (sequential)	Encapsulation drives skin/core formation
Somnuk and Smith [1995]	Two channel (simultaneous)	Good mould filling results for $\eta_{\text{skin}} \approx \eta_{\text{core}}$ (0.8-1.8), $\text{velocity}_{\text{skin}} \approx \text{velocity}_{\text{core}}$
Young et al. [1980]	Single channel (sequential)	$1.5 \leq \eta_{\text{skin}}/\eta_{\text{core}} \leq 2.0$ led to uniform skin thickness.
Cheng et al [1995]	Single channel (sequential)	Melt flow occurring in the region of the gate during the post-filling.
Lee et al [1998]	Two channel (simultaneous)	Injection speed and simultaneous length most important processing parameters

Table 3-1 Summary of relevant research in co-injection moulding of compatible materials

The study by Young et al. [Young, 1980] used immiscible PS and PP components as the skin and core materials. However the study looked only at relative skin /core distribution rather than their immiscible nature. The viscosity of several materials was measured at zero shear and then combinations of these materials moulded, but always using equal amounts of skin and core material. There was major breakthrough when the lower viscosity PS core jets through the much higher viscosity PP skin and poor penetration of the much higher viscosity PP core into the lower viscosity PS skin. There was much better mould filling when both materials had nearly the same viscosities, or when the core material was slightly more viscous. It was also found that better

mouldings could be obtained by increasing the amount of core material when the skin viscosity was too low.

From injection moulding it is well known that both the temperature of the mould and the speed at which the materials are injected into the mould cavity also determine the end structure. This was detailed in Chapter Two. The temperature of the mould will affect the rate at which the skin material will freeze, the greater the difference in temperatures of the skin and mould surface the more quickly the material will solidify. The rate at which the skin material is injected will determine how much time the leading edge of the skin material will have in contact with the mould surface. A greater speed would lead to the skin material penetrating further into the mould. In relation to these parameter effects in co-injection moulding Akay [Akay, 1983] found that increased injection speeds of skin material could prevent breakthrough. This was especially true at low mould temperatures, but as speeds increased so too did instabilities in the flow. These instabilities could result in a better interfacial region between skin and core material. However, taken to extremes these instabilities could also cause breakthrough in the mouldings.

Zoetelief [Zoetelief, 1995], claimed that fountain flow governs the breakthrough of the core material and that material distribution can be best controlled through moulding simulation. The importance of simulation was also reinforced in the work of Somnuck, [Somnuck, 1995] and a simple model was developed for setting co-injection moulding parameters. Somnuck tested a number of viscosity ratios within a number of different mould designs to discover how

much material could be included in the core of a moulding and what ratios provide optimal results. It was found that the most uniform core distributions were achieved at ratios of skin to core between 0.80 and 1.83. With these ratios about 60% core could be concealed within a square flat plaque moulding without breakthrough, and about 70% core in a disk mould. However, this work was based on research using PP as both skin and core.

Lee et al. [Lee, 1998] based studies within this viscosity ratio band to develop a model that could predict the material interface in simple geometry mouldings. After the choice of viscosity ratio, the variables in the process that have the greatest effect on the interface are the injection rate and the length of simultaneous injection. Too short an interval between the injection of skin and core can result in breakthrough, too long and too much skin is forced to the outer edges of the moulding.

3.5 *Simulation: limitations*

The importance of simulation has been noted by a number of researchers. Computer simulation is available for flow analysis during co-injection moulding. An example is C-Mold .The program can analyse the flow of material into a mould cavity from the skin and core and estimate the skin/ core ratios as well as show when core breakthrough is likely to occur in the finished component. However there are several discrepancies between predicted and actual filling processes that occur during co-injection moulding [Rungseesantivanon, 2000] and surface defects such as ridges and instabilities are also not predicted on current C-Mold software.

3.6 Elastic Properties of melts

Most polymers are viscoelastic, this property being used to good effect in processes such as blow moulding and thermoforming. The viscoelastic properties help to regulate the wall thickness of these production routes. In shear flows such as extrusion however, viscoelastic instabilities can occur which are responsible for extrudate distortions such as sharkskin and surface distortion found in calendering operations. These types of effects will be further examined in Chapter 4.

3.6.1 Molecular effects

If a constant velocity is applied on a polymer and then stopped, the polymer will not respond or not go back to zero stress instantaneously as shown in Figure 3-8. These are known as retardation and relaxation phenomena. They are commonly of the same magnitude and denoted by the symbol θ .

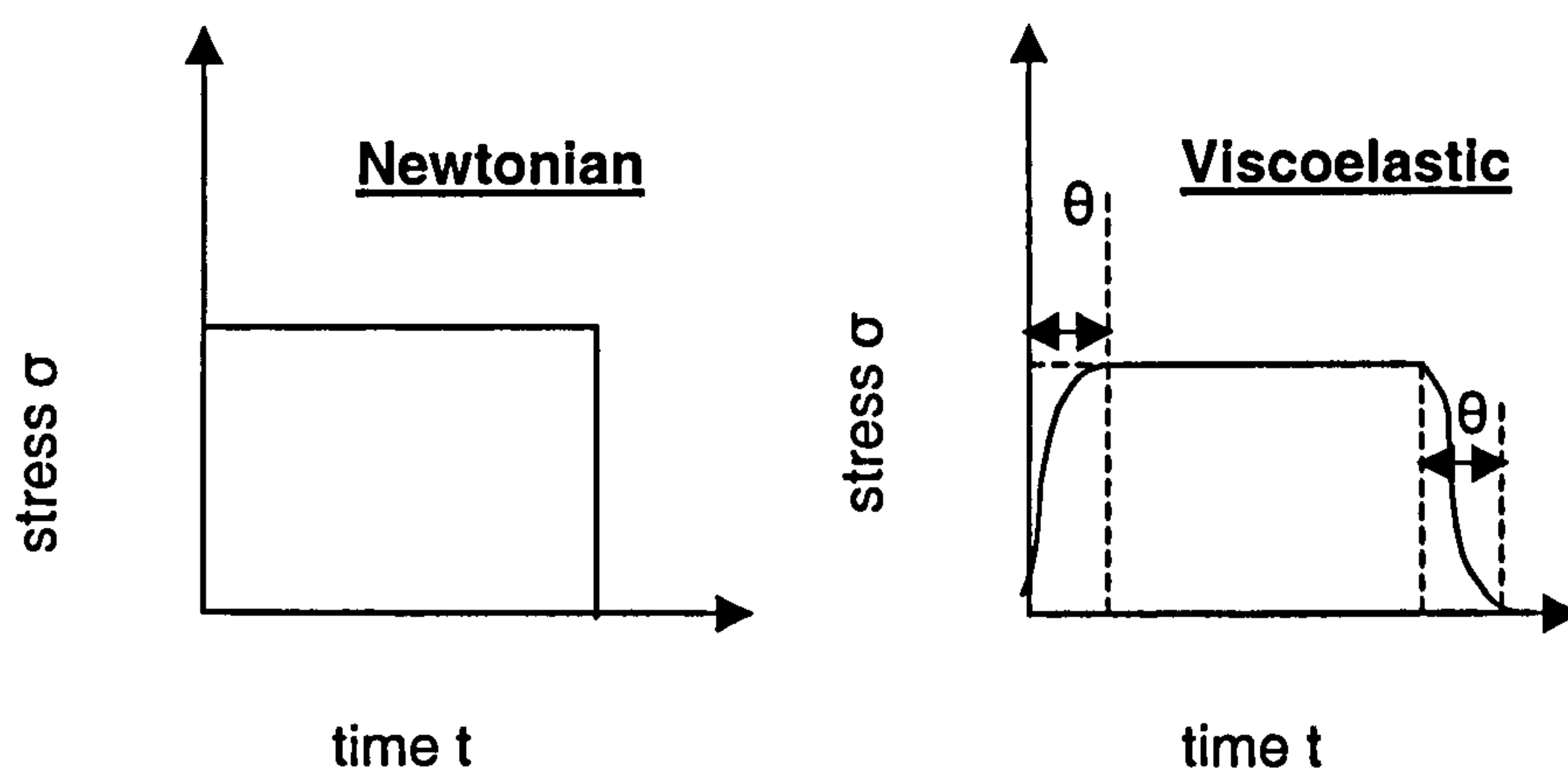


Figure 3-8 Stress growth and relaxation [Aggasant, 1991]

The diagram as represented by the authors in Figure 3-8 is somewhat misleading in terms of stress growth, as it is likely that during shear thinning behaviour the largest stress will be actually be the initial force required. Therefore, this diagram would be better if it showed a drop in stress during the initial period.

The relaxation time of a polymer melt is the time required for a change in molecular configuration. Typically for polymer melts this will be in the range 10^{-2} - 10^2 s [Agassant, 1991]. A dimensionless number of use in assessing likely elastic effects is the Deborah number, which is a ratio of fluid characteristics and the time of flow , such as a residence time.

$$De = \theta/t$$

Equation 9

where θ = fluid characteristic time, t = characteristic time of the flow

If $De \gg 1$, behaviour is elastic, if $De \ll 1$, elasticity is insignificant.

3.6.2 Deformation processes

The response of polymer flows during injection moulding to deformation processes is a complex mixture of shear, extension and bulk deformations [Cogswell, 1996].

Stresses can occur in a number of directions as shown in Figure 3-9. Representations such as these are often used to show the force balance on an element [Agassant, 1991]. There are three components of normal stress (xx , yy and zz on Figure 3-9) and six components of shear stress, giving a total of nine stresses using this method of analysis.

Shear flow is produced when stress is applied tangentially. Extensional flow is the result of stress applied normal to the surface of the material and bulk deformations result when stress is applied normal to all faces.

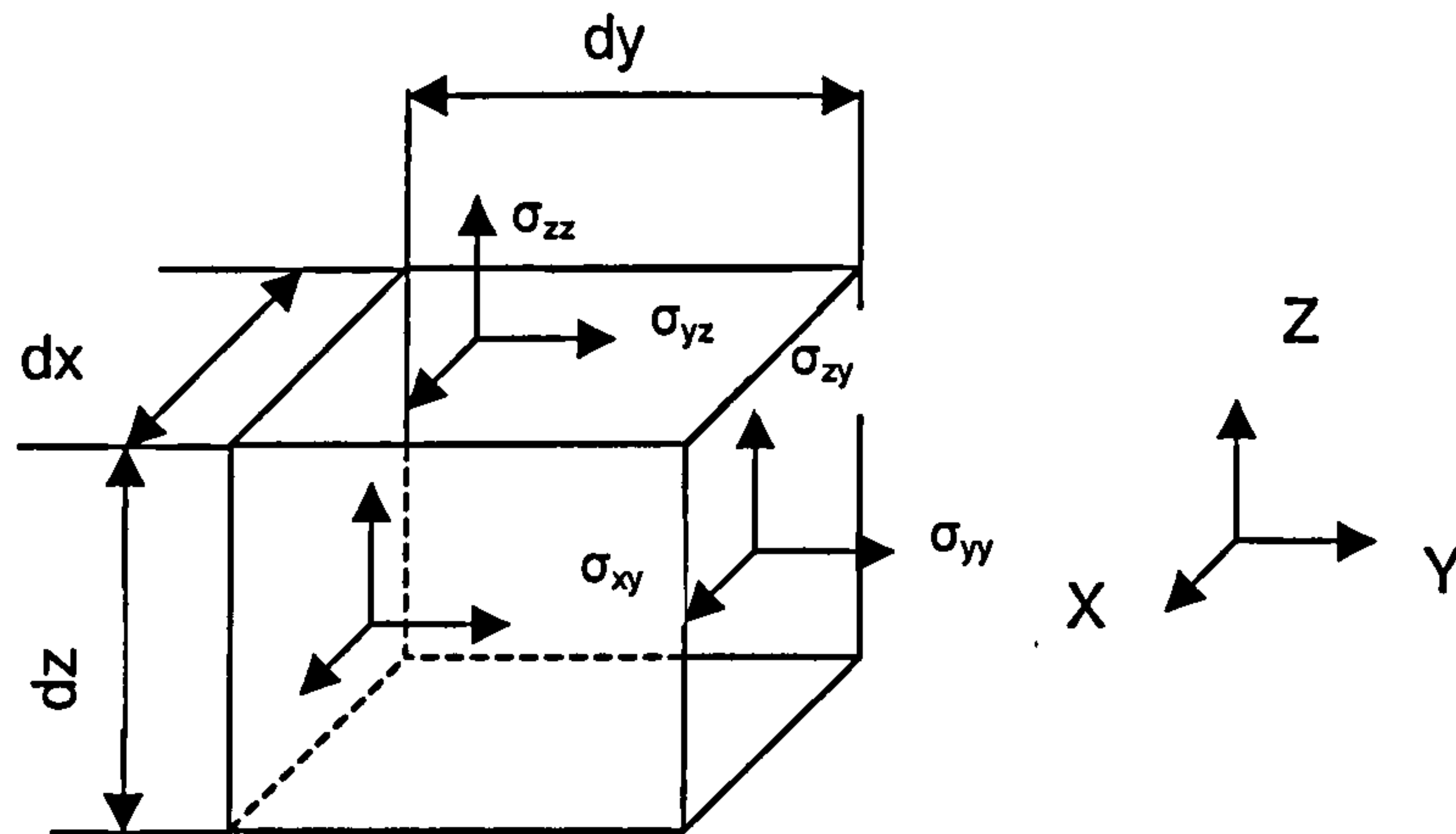


Figure 3-9 Possible stresses on an element

During shear flow, polymer chains are deformed and orientate in the direction of flow. The tension of the polymer in the flow direction is called the first normal stress [Agassant, 1991]. In contrast to this, flow in other directions is relatively small. First normal stress can be defined by the difference between the normal stress component in the flow direction and the normal component in the direction of the shear plane [Agassant, 1991].

3.7 Conclusion To Literature Review

Several studies in sequential and simultaneous co-injection moulding have revealed that the viscosity ratios between the core and skin materials have a major impact on the interface of the materials within the moulding. An ideal ratio range has been suggested at which to conduct moulding, and studies suggest that the injection rate and length of simultaneous injection are the next variables that have the greatest effect on the end structure.

Skin/core viscosity relationships in co-injection moulding appear to have fascinated researchers since the seventies. Only with the advent of mixed material studies such as those by Akay, Selden, Rungseesananantivanon and Goodship, each of whom was introduced in Chapter 2, has interest been shed on the complex mechanisms occurring at the interface. These studies have indicated that a rheological explanation for such effects is insufficient on its own to explain the interfacial effects that are observed with increases in injection speed appearing key to these studies.

In concentrating on material distribution, the effects of co-injection moulding on the material morphology and properties have also been ignored. Further, the work of Selden and Rungseesananantivanon on compatibilised systems has also ignored bulk properties in favour of measuring interfacial bonding and skin/core thickness, which this research will find inadequate in terms of the failure to describe the bulk weakness inherent in these mouldings.

Finally, it appears all previous research in this area has ignored the fact that polymers have both viscous and elastic components. Given the high shear

rates employed during injection moulding and the relationship between increases of elasticity with shear, it seems reasonable to assume that elastic effects will occur. The importance of injection speed has been highlighted by Goodship, Akay and Selden. It can be postulated that an increase in injection speed would bring about an increase in shear and therefore also increase elastic property effects in the mouldings.

Despite the lack of literature relating to instabilities in co-injection moulding, there is a large body of work relating to instabilities in other polymer processes. The next chapter will examine their findings and attempt to relate these studies to the effects seen during co-injection moulding of two polymers.

Chapter 4. Instabilities in Polymer Processing

4.1 *Introduction*

The viscoelastic nature of polymers produces instabilities entirely absent from Newtonian fluids. Instabilities are caused when laminar flow is disturbed and have been known to occur in a number of processes including film blowing, fibre spinning and extrusion [Petrie, 1976].

A number of reviews of viscoelastic instabilities have been produced [Petrie, 1976], [Tanner, 1985], [Larson, 1992]. However, as shown previously little work has addressed instabilities associated with the co-injection moulding process. These studies have already been highlighted in Chapter Two.

The process that seems most appropriate to compare to studies of co-injection moulding is co-extrusion. Like co-injection moulding, co-extrusion has two stratified materials flowing together. There are however some major differences that need to be considered. For example, co-extrusion is carried out at much lower shear rates and without the same kind of temperature, pressure and shear gradients experienced in the injection moulding process. It was seen in Chapter Three that material characteristics such as viscosity can vary greatly depending on the value of these parameters. In co-injection there is also a point where the skin/core materials meet at the flow front, again

absent in co-extrusion. This makes the study of instabilities in injection moulding considerably complex.

The banded laminated structures in co-injection moulding identified by Akay [Akay, 1983] and Selden [Selden, 1998] do not appear in co-extrusion literature. Since their appearance appears to be linked to the use of high injection speeds, it could be that co-extrusion processing does not generate such high levels of shear to generate such effects. However if the cause of instabilities is elastic in nature, it is possible that instabilities in other processes such as co-extrusion could offer clues to the cause of co-injection instabilities. Therefore a brief review of some pertinent studies is given in 4.3. However, before that a brief introduction to the Reynolds Number is required.

4.2 *Reynolds Number*

The change from laminar to turbulent flow can be described by the Reynolds number (Re). This dimensionless number was derived from research on water flow through a tube performed by Reynolds in 1883. It is a measure of the relative importance of viscous and inertial forces. According to classic hydrodynamic theory, flow becomes turbulent when Re is larger than a characteristic number usually between 2,000 and 10,000 [Acheson,1990].

In flow through a slit of thickness h , and for an average velocity U , of a fluid of kinematic viscosity, ν , the Reynolds number is given by Equation 10.

$$Re = \frac{Uh}{\nu}$$

Equation 10

If we consider injection moulding we can define:

$$U < 1\text{m/s}, h < 3\text{mm}, \nu > 0.1\text{m}^2/\text{s}$$

giving Re well below 0.1. This means that inertial forces are negligible and at such low Reynolds numbers there should be no sign of turbulence in the melt stream.

4.3 *Instabilities of multi-layer flows*

The practical application of multiple polymer layers include co-extrusion and multi-layer coating. In applications such as these, uniformity of the layers is required and avoiding instabilities is of major importance.

In co-extrusion, instabilities occur because of stratification of fluids properties such as density, viscosity or elasticity [Renardy, 1987]. A jump of first normal stress across the interface in one or both elastic fluid can also cause instability, even with matched viscosities and densities and a Reynolds number of zero [Chen, 1991]. This would suggest that despite the low Reynolds number in injection moulding, instability could also occur in injection moulding if normal stress differences were occurring. Also in co-extrusion a normal stress jump can be either stabilising or destabilising depending on the volume ratios of the components. Again, this suggests loading levels of skin and core components could be important in this research. If the more elastic fluid occupies less than half the channel it is destabilising, otherwise it is stabilising. Khomani

[Khomani, 1990], found that interfacial instability is sensitive to shear thinning behaviour in the less viscous layer.

4.4 Conclusions

If the experiments in co-extrusion can be related to the co-injection moulding process it appears instabilities may occur under the following conditions:

- Stratification of fluid properties such as viscosity or elasticity:

Stratification of properties appears to be the most obvious cause of instabilities since it is also interesting to note that a body of literature exists relating to what appears to be instabilities in single injection moulding. For example Hobbs [Hobbs, 1996], examines gloss variations in resin blends which interestingly also take on a banded like structure similar to that reported in co-injection moulding studies. These defects are reported to be the result of slip/stick flow at high shear rates causing the resin surface to be highly stretched and deformed in the direction of flow. Dharia [Dharia, 1999] also found that polyolefin blends produced 'tiger stripe' regions on the mouldings. Both molecular weight and relaxation behaviour were found to be critical determinants to this behaviour which suggest some kind of stratification of properties is occurring within the molten flow.

- Layer ratios

The relative amounts of material in the skin/core also appears to be a factor, as reported previously if the more elastic fluid occupies less than half the

channel it is destabilising. Any shear thinning in the less viscous layer must also be considered in terms of producing unstable structures.

4.5 *Summary of literature review*

Summing up the findings from Chapters 2, 3 and 4, the literature has revealed several likely possibilities for investigations into surface defects and instabilities associated with the co-injection moulding process. These being:

- Statification of fluid properties such as :
 - ❖ Density, viscosity or elasticity (first normal stress).

- Injection Speed

It appears injection speeds and the associated increase in shear are also implicated in instability formation.

- Viscosity Ratio

The effect of initial skin/core viscosity ratios is hard to ascertain at this stage, however the mechanism of encapsulation is of key consideration.

Various researchers [Somnuk, 1995], [Lee, 1998] give a useable viscosity ratio range of 0.8-2.0 for skin and core.

- Layer ratios

A number of researchers [Selden, 1998], [Rungseesantivanon, 1999] report varying skin thickness being thinnest at gate area. This could be the result of shear thinning in the less viscous layer. Lower speeds are reported to give a more uniform distribution. Co-extrusion studies show that the relative amounts of skin/core can also have either a stabilising or a destabilising effect.

With this knowledge in mind an investigation into both the ridge effect and the poorly understood mechanisms of co-injection moulding can begin. The objectives of this research are outlined below.

- Determine the extent to which the interfacial surface distortion extends and to the material systems to which it applies.
- Investigate the mechanisms that cause the surface distortion at the melt front interface.
- Determine processing conditions to eliminate the surface distortion effect.
- Develop a process route for the use of immiscible materials that eliminates the aesthetic defect and hence remove some of the limitations in the use of various combinations of immiscible materials mouldings.

Chapter 5. Experimental Overview and Miscible Systems : Experimental Method and Results

5.1 Overview

All mouldings produced for this study were produced on a Battenfeld co-injection moulding machine series BMT-1100/2x300 controlled with the UNILog 9000. The specification of this machine is given in Table 5-1.

Machine Design	Two-stage, hydraulic clamping system with swing disc	
Clamping unit	Clamping force, max.	1100 kN
	Opening force, max.	94 kN
	Space between tie-bars	470 mm
Hydraulic ejector	Ejection force, max.	44 kN
	Ejection stroke, max.	160 mm
Injection unit	Injection force, max.	238 (2x) kN
	Screw stroke, max.	125 (2x) mm
	Nozzle contact force, max.	187.6 kN
	Nozzle stroke, max.	270 mm

Table 5-1 The Battenfeld BMT-1100/2x300 machine specification

5.1.1 Preliminarily moulding

An initial set of mouldings sought to look at whether the ridge effect identified in Chapter One was a peculiarity of the Nylon/ PP systems or was applicable to other co-injection moulding systems. Ten variations were chosen based on the availability of material on site. No account was taken of the individual rheology of the material at this initial stage although the importance of rheology

has been introduced and noted in Chapter Three and will be of importance in later experiments. The samples are detailed in Table 5-2.

Combination Number	Skin Material	Core Material	Miscible/Non-Miscible (M/N)
1	PA6	PP	N
2	PA12	PP	N
3	PP	PA12	N
4	PP	HDPE	N
5	HDPE	PP	N
6	PS	HDPE	N
7	HDPE	PS	N
8	HDPE	LDPE	M
9	LDPE	HDPE	M
10	PP	PP	M

Table 5-2 Material Combinations for Initial Study

A ridge was considered to be present if a surface distortion could be easily seen at the skin/core interface by looking under a light. This is a common method for visually judging surface appearance [Lloyd, 1999]. Surprisingly, given the apparent lack of literature relating to this effect, the defect could be found or induced in all samples. Injection speed and core injection delays were the parameters used to induce ridges. Therefore, this implies there is a mechanism of ridge formation applicable not just to the Nylon/PP system but to a group of material combinations for co-injection moulding under certain parameter conditions including PP/PP systems. This is a novel finding.

Co-injection moulding literature offered no clues as to the cause of the ridge, the only mention of the ridge in literature is by the author [Goodship, 2001, a], reporting its presence in a PA12/ PP compatibilised system. This could suggest that previous researchers have overlooked ridge type defects as their

interests lay in other areas. Alternatively, the effect may be related to a peculiarity in the set up of the machine or tool design. However, if it was a more widespread phenomenon, a surface defect of this kind would have major implications for commercial exploitation of these technologies especially for components requiring good aesthetics. The next step therefore was to identify the factors involved in the ridge creation.

The geometry and gating of the tool were not unusual: a centre gated sprue plaque as shown in Figure 5.1.

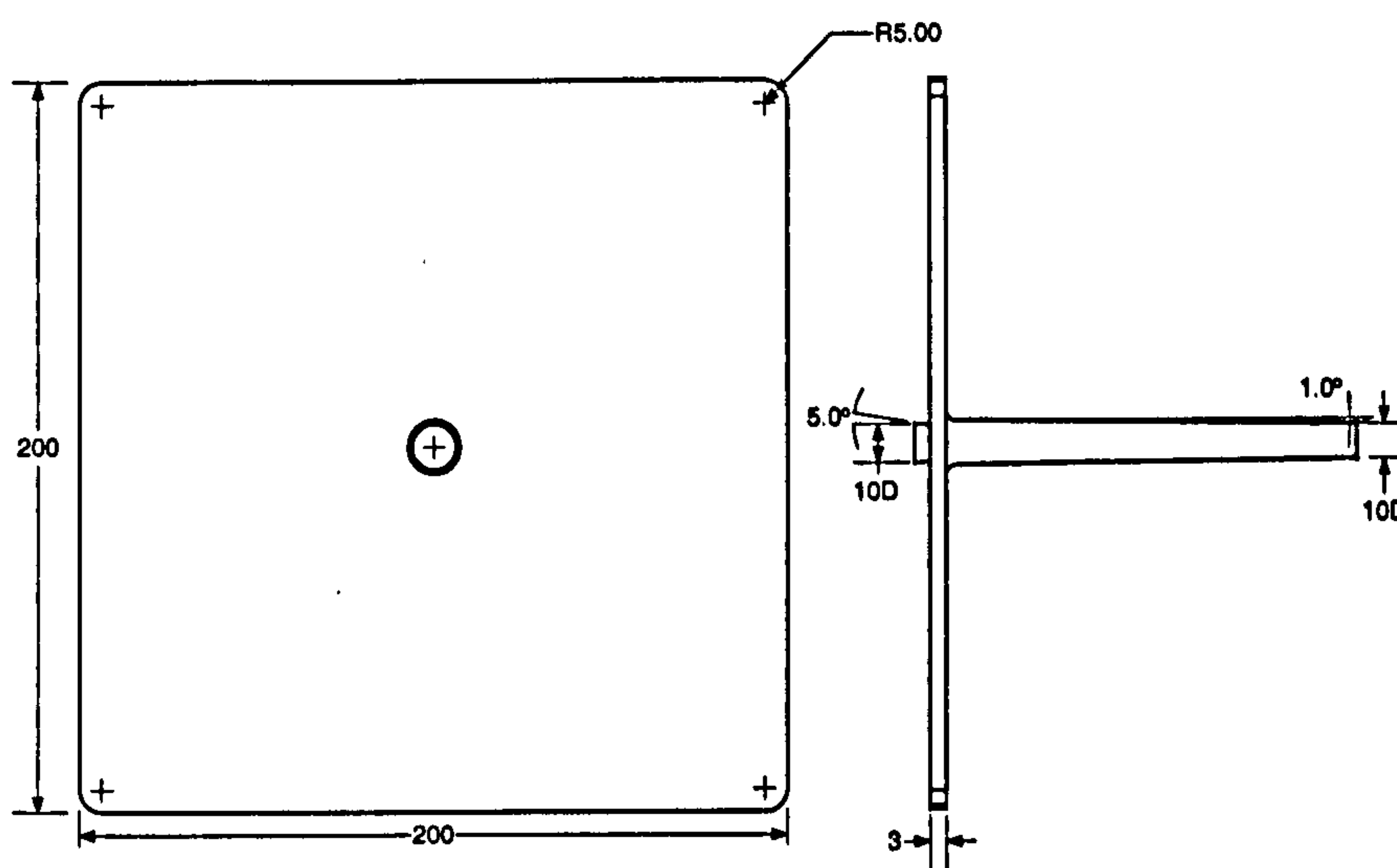


Figure 5-1 Centre gated square plaque tool

However, the effect being tool related could not be ruled out at this stage. It was clear from this simple scoping study that both miscible and immiscible material groups needed to be considered. Therefore, the next experiments were split into three groups to compare the effects of various combinations of miscible, compatibilised and immiscible mouldings. Moulding trials were

carried out as detailed in each of these three experimental sections and specimens examined using methods most appropriate to the material systems in question. Experiments and results for the compatibilised and immiscible systems are set out and discussed in chapters seven and eight.

5.1.1.1. Shrinkage

One obvious cause of the ridge was quickly eliminated, that being shrinkage differences between skin and core materials. It was found changing material position, that is switching which material was skin and which was core, did not affect the ridge. It was always present during visual examination as described previously. If shrinkage were indeed the cause of the defect, it would be expected this switch would produce a dip instead of a ridge. This effect is illustrated in an exaggerated manner in Figure 5-2. However, this was not the case in any combination of mouldings shown in Table 5-1. Whilst shrinkage differences are important in terms of overall moulding performance, in terms of the ridge defect this effect is negligible.



Figure 5-2 Expected effect of shrinkage on ridge of reversal of skin/core position

5.1.1.2. Processing effects

It was hoped relating the mechanical properties of standard injection mouldings to co-injection moulding would reveal any processing-property differences that exist between the two types of moulding and provide answers to possible causes of ridge type defects. However, data relating the mechanical properties of standard injection mouldings to co-injection moulding tends to be concentrated on recyclate research [Donovan, 1975], [Cain, 2000], [Goodship, 2001, c]. Often single injection mouldings are used as a datum to compare the properties of the co-injection moulded specimens. Research of this type has commonly been focused on the amount of recyclate that can be incorporated into the core and its properties rather than investigating any differences inherent in the two moulding systems. It appears to have been assumed by researchers such as Donovan et al and Cain et al, that with the same material, there would be no difference in properties between specimens produced by single and co-injection moulding and that any property effects were related to the materials not the process. In order to test this assumption, a series of experiments were performed in order to compare these two methods. As the following experiments will show the injection method does affect the properties of the moulding.

5.2 Mechanical Properties of Polypropylene Mouldings

5.2.1 Testing Justification

Due to the large number of samples produced during these experiments, mechanical property testing needed to be limited. At least ten mouldings were produced for each parameter setting and five tensile specimens were randomly

selected from these. Standard deviations were low for each test, justifying that only five samples were used.

The choice of tensile testing was due to two factors. Firstly, to determine whether there would be any difference in tensile properties in injection mouldings and co-injection mouldings since little data was available. Secondly the values for ultimate tensile stress, modulus and elongation could be produced from a single test and these represent three different properties of strength, stiffness and ductility. A single crosshead speed for all tests was essential owing to the viscoelastic nature of polymers which means at higher crosshead speeds the material can appear stiffer than when tested at lower strain rates.

The general lack of literature on tensile properties relating to co-injection moulding can be attributed to the fact that there is relatively little research in any area of co-injection moulding. Although it has been around since the seventies it is only fairly recently that the associated advantages of this technique, for example in incorporating recyclate and for added value manufacturing are being recognised. Secondly, co-injection was initially developed to provide an improved surface skin for foamed products, therefore subsequent published research has concentrated on the fact that the properties of co-injection mouldings are reliant on the surface material alone. However, the choice of flexural testing by other researchers whilst offering comparative quality control say nothing about the intrinsic material properties of co-injection mouldings. The nature of a bending test, that being, one side in tension and the other in compression as well as leaving the neutral axis in the area of the core material, also introduces some transverse shear component to the test piece.

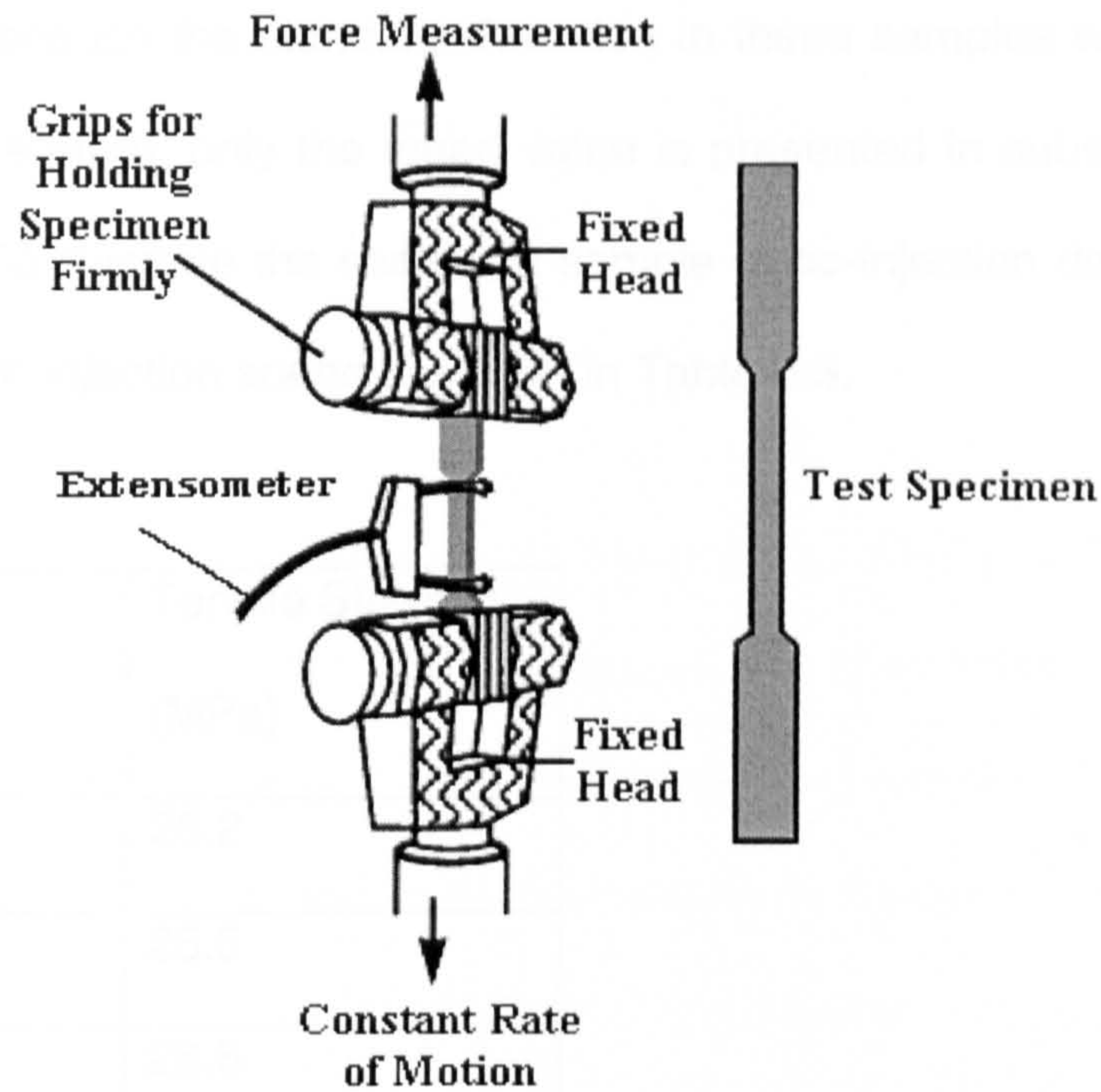


Figure 5-3 Tensile testing [Han, 1992]

Tensile testing is the most important method for measuring static tensile strength and ductility [Han, 1992]. A standard specimen is loaded uniaxially in tension. The resulting stress-strain data enables several important parameters to be obtained such as tensile strength at break and modulus of elasticity (rigidity). In these tests an extensometer was attached as shown in Figure 5-3 to also measure elongation to break.

5.2.2 Mechanical Testing Method

Tests were carried out using an Instron Model 4505 Universal testing machine equipped with series IX automated materials testing software. Testing was carried out in accordance with BS 2782 method 320A, (this has now been superseded by ISO527), using an external extensometer to measure strain. Five samples were randomly selected for tensile testing. This is the minimum number of samples specified in the standard, but this was considered

acceptable because the standard deviation in these samples was low at less than 1%. Therefore, only the mean value is presented in subsequent results summaries. To illustrate the scatter, a sample of co-injection data, taken from experiments in injection speed is shown in Table 5-3.

	Tensile Strength (MPa)
1	26.2
2	26.5
3	26.6
4	26.8
5	26.4
Mean	26.5
S.D.	0.2

*Table 5-3 Sample results for co-injection moulding experiments
(the result summary is shown in Table 5-16)*

The rest of this chapter outlines the experiments and procedure relating to the investigation of miscible systems of polypropylene skin and core.

5.3 Experiments for Miscible System: comparison of the single injection moulding and the co-injection moulding system

5.3.1 Tooling

The mould used was a “dogbone” tool designed to meet British Standard BS 2782: Part 3: Method 320C, Determination of Mechanical Properties for Plastics. The tool allows two components to be produced in a single shot. This tooling was used instead of the tool shown in Figure 5-1. The mouldings produced are ready to use tensile specimens without requiring milling. This removes any errors that may be incurred in taking samples from different areas of a larger moulding such as the square plaque. Since this experiment seeks only to consider the difference inherent in single injection to co-injection process effects, as a basis for further investigation into the ridge effect, the tooling change is not significant. The direction of mould filling can be seen in Figure 5-4.

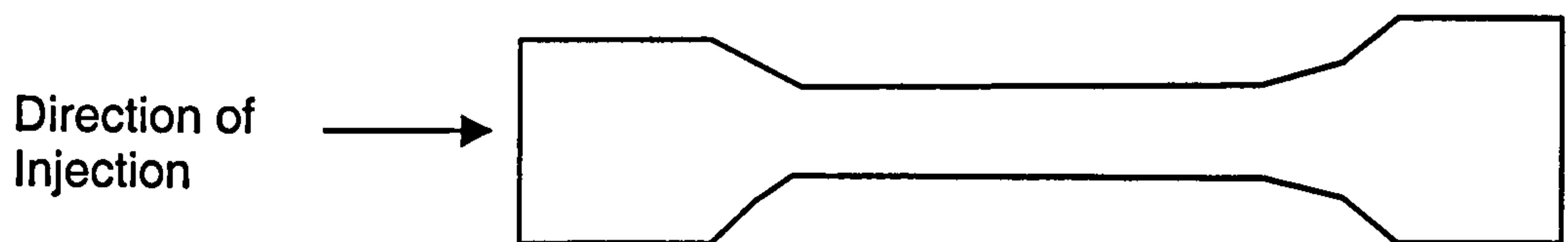


Figure 5-4 Filling direction for “dogbone” tool.

5.3.2 Material

The material used was DSM copolymer polypropylene Stamylen P56M10 MFI 6.2. This is a commodity grade used in large quantities in industrial production. For the co-injection mouldings, the core material was coloured red with a low

dosage (1%) of a commercially available red masterbatch. This allowed the skin and core to be visually distinguished.

5.3.3 Experiment 1 :Effect of processing parameters on single injection polypropylene

5.3.3.1. Processing Parameters

A standard set of processing conditions were found producing good quality and consistent components these conditions are shown in Table 5-4.

Moulding Parameter	Setting
Melt Temperature	220°C
Mould Temperature	40°C
Back Pressure	5 bar
Injection Speed	100 mms ⁻¹
Holding Pressure	20 bar
Holding Time	15 bar
Cooling time	30 sec
Metering Stroke	35mm

Table 5-4 Standard processing parameters for Experiment 1

The values of these parameters were adjusted one value at a time whilst the other conditions were kept constant. The variable conditions set for each parameter are shown in Table 5-5.

Parameter	Setting				
Melt temperature (°C)	180	200	220	240	260
Mould temperature (°C)	20	30	40	50	60
Injection speed (mms ⁻¹)	50	100	150	200	250
Holding pressure (bar)	10	20	30	40	50
Holding time (sec)	5	10	15	20	25

Table 5-5 Processing variables for Experiment 1

Experimental Procedure.

With the exception of temperature, all the combinations of parameters listed in Table 5-5 were processed randomly to eliminate any order effects. When material parameters were changed the first five mouldings produced were discarded. The temperature tests were done separately again in a random order allowing 15 minutes for temperature changes to take effect. Material was purged from the machine at this time to eliminate any degradation effects and the first five plaques discarded.

5.3.4 Result Summary: Single Injection Moulding

5.3.4.1 Experiment 1: Single Injection

Melt Temperature (°C)	180	200	220	240	260
<i>Tensile Strength (MPa)</i>	25.8	24.2	25.5	24.0	24.8
<i>Young's Modulus (GPa)</i>	1.7	1.5	1.5	1.4	1.4
<i>Elongation (%)</i>	54.2	54.3	55.6	55.0	55.8

Table 5-6 The Effect of melt temperature on the mechanical properties of single injection PP

Mould Temperature(°C)	20	30	40	50	60
<i>Tensile Strength (MPa)</i>	25.5	25.2	25.5	25.8	26.2
<i>Young's Modulus (GPa)</i>	1.7	1.7	1.5	1.6	1.5
<i>Elongation (%)</i>	54.5	54.8	54.6	54.5	55.1

Table 5-7 The effect of mould temperature on the mechanical properties of single injection polypropylene

Injection Speed (mms⁻¹)	50	100	150	200	250	290
<i>Tensile Strength (MPa)</i>	26.5	26.2	25.5	25.8	26.7	25.6
<i>Young's Modulus (GPa)</i>	1.6	1.6	1.5	1.5	1.5	1.3
<i>Elongation(%)</i>	56.5	56.8	58.3	59.1	58.4	58.6

Table 5-8 The effect of injection speed on mechanical properties of single injection polypropylene

Holding pressure (bar)	10	20	30	40	50
<i>Tensile Strength(MPa)</i>	25.5	25.2	25.5	26.8	25.5
<i>Young's Modulus (GPa)</i>	1.5	1.6	1.5	1.6	1.5
<i>Elongation(%)</i>	56.7	56.8	56.1	56.6	56.1

Table 5-9 The effect of holding pressure on the mechanical properties of single injection polypropylene

Holding Time (secs)	5	10	15	20	25
<i>Tensile Strength (MPa)</i>	27.5	26.2	25.5	25.8	26.5
<i>Young's Modulus (GPa)</i>	1.6	1.5	1.4	1.6	1.5
<i>Elongation(%)</i>	54.9	56.5	55.1	55.1	55.3

Table 5-10 The effect of holding time on the mechanical properties of single injection polypropylene

5.3.5 Experiment 2 : Effect of processing parameters on co-Injection polypropylene

Processing Parameters:

A standard set of processing conditions were found which produced good components these conditions are shown in Table 5-11.

Moulding Parameter	Setting
Melt Temperature Barrel A	220°C
Melt Temperature Barrel B	220°C
Mould Temperature	40°C
Injection Speed Barrel A & B	100 mms ⁻¹
Holding pressure (on B)	20 bar
Set point	8mm
Holding time	10 sec
Cooling time	30 sec
Metering stroke Barrel A	19.7 mm
Metering stroke Barrel B	23.1 mm
Injection delay on B	0.1 sec
Back pressure A & B	5 bar

Table 5-11 Standard process parameters for Experiment 2

The values of these parameters were adjusted one value at a time whilst the other conditions were kept constant as above. The 5 variable conditions set for each parameter are shown in Table 5-12.

Parameter	Setting				
Melt temperature A& B (°C)	180	200	220	240	260
Mould temperature (°C)	20	30	40	50	60
Injection speed A & B (mms⁻¹)	50	100	150	200	250

Table 5-12 Variable settings for Experiment 2

Since these experiments concern co-injection moulding, the relative speeds of the skin and core to each other were also varied. These are shown in Table 5-13.

Parameter	Number	1	2	3	4	5	6	7
Injection Speed A: skin (mms ⁻¹)		150	100	50	200	200	290	290
Injection Speed B: core (mms ⁻¹)		100	50	25	150	25	150	280

Table 5-13 Skin/core variable speed settings for Experiment 2

Experimental Procedure: as per Experiment 1

5.3.6 Results Summary : Co-Injection Moulding

Melt Temperature (°C)	180	200	220	240	260
Tensile Strength (MPa)	26.8	25.2	25.5	26.0	25.8
Young's Modulus (GPa)	1.9	1.8	1.7	1.6	1.6
Elongation(%)	8.3	8.0	9.8	9.5	10.2.

Table 5-14 The effect of melt temperature on the mechanical properties of co-injection polypropylene

Mould Temperature (°C)	20	30	40	50	60
Tensile Strength(MPa)	25.5	25.2	25.5	25.8	26.2
Young's Modulus(GPa)	1.9	1.7	1.5	1.6	1.6
Elongation(%)	9.7	10.1	10.2	12.0	11.7

Table 5-15 The effect of mould temperature on the mechanical properties of co- injection polypropylene

Injection Speed A/B (mms ⁻¹)	50 / 25	100 / 50	150 /100	200 /150	200 / 25	290 / 150	290 / 280
<i>Tensile Strength (MPa)</i>	26.5	27.0	26.6	27.0	26.5	26.8	27.3
<i>Young's Modulus (GPa)</i>	2.1	2.0	1.9	1.8	1.9	1.9	1.9
<i>Elongation (%)</i>	34.7	40.6	40.3	40.9	48.4	36.8	33.57

Table 5-16 The effect of injection speed on mechanical properties of co-injection polypropylene

5.3.7 Scanning Electron Microscopy

The polymer microstructure of selected mouldings from both polypropylene experiments were evaluated in a qualitative fashion by use of a scanning electron microscope. Samples were selected to consider extremes of parameter variations and compared to the standard processing plaques. The equipment used was a Cambridge Stereoscan 90. Samples were mounted on stubs and sputter coated with a thin layer of a gold/palladium alloy. This is necessary to ensure a continuous charge path during microscope operation. The results of this analysis are shown in the next Chapter

Chapter 6. Discussion on Miscible Systems

The experimental program was divided into sections whereby each topic could build on the results of the previous experiments. These sections can be categorised under the following headings.

- Extent of surface defect problem common to all systems
- Identifying mechanisms of surface distortion
- Determine optimum process conditions
- Developing a process route to eliminate surface distortions

This chapter covers the first two of these objectives, with later experiments and discussion building on these results.

6.1 Extent of surface defect problem common to all systems

The preliminary moulding detailed in Chapter Five aimed to determine whether the ridge was a result of a mechanism unique to the compatibilised Nylon/ PP system or whether the defect was in fact applicable to a number of material systems. Experiments revealed the ridge to not only be applicable to immiscible systems but could be induced even in PP/ PP systems. This is a novel finding and makes this work applicable to a wide range of material co-injection moulding systems. The next step therefore was to identify the factors involved in the ridge creation. Shrinkage was eliminated as a cause and attention focused on differences which may be occurring due to a difference in the processing methods of co-injection moulding and single injection moulding.

Mouldings were produced and tested for mechanical properties. These results will now be evaluated.

6.1.1 Tensile strength

The initial set of experiments investigated the mechanical strength of single injection moulded specimens versus co-injection moulded specimens. The parameters chosen to examine were based on the findings from the literature survey. Therefore the parameters chosen were the influence of injection speed, packing time, packing pressure, melt temperature and mould temperatures on properties. The simultaneous phase was not studied in its own right, since variations in skin/core loading speeds would also mean the simultaneous phase would alter accordingly. Tensile strength results for standard injection mouldings are shown in Tables 5-6 to 5-10 and mirror the investigations of Stidworthy [Stidworthy, 1999]. He also surprisingly found for polypropylene that processing parameters had little influence on mechanical strength. Co-injection mouldings also showed little variation in strength characteristics, results are shown Tables 5-14 to 5-16 and are summarized in Figures 6-1 and 6-2. It should be noted that all moulding parameters are plotted on the same dimensionless axis corresponding to their numerical value.

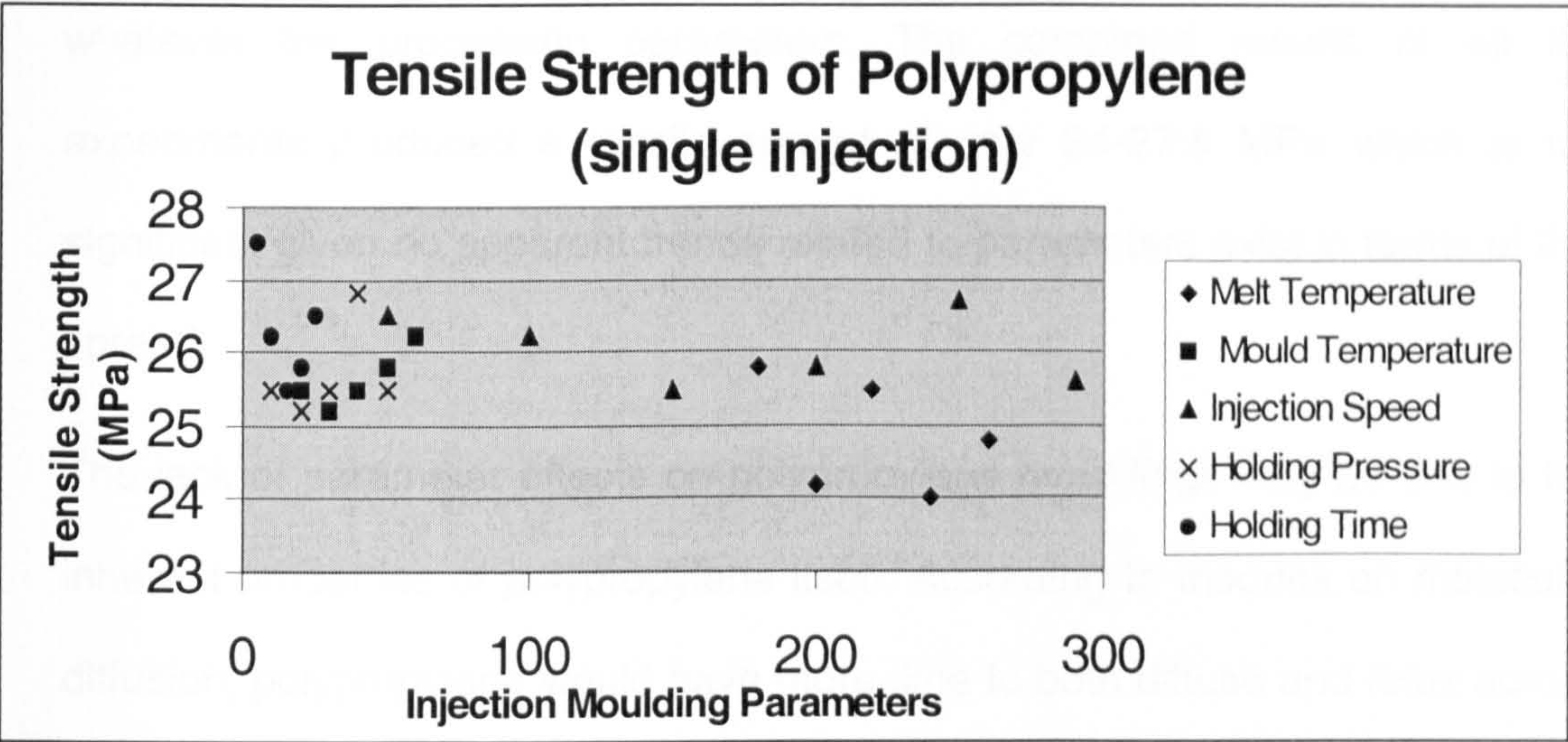


Figure 6-1 Effect of parameter changes on polypropylene injection mouldings

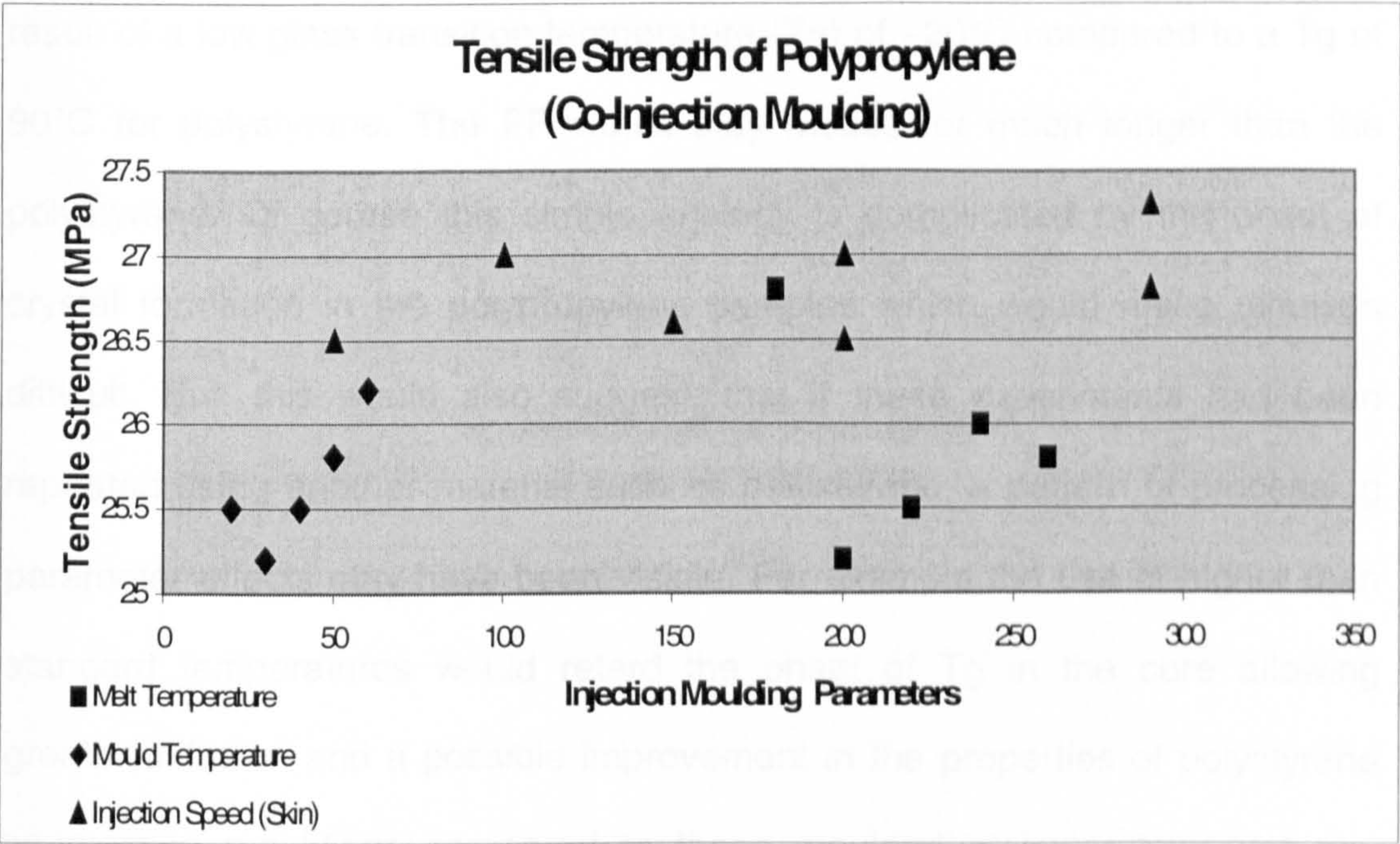


Figure 6-2 Effect of parameter changes on polypropylene co-injection mouldings

Figures 6-1 and 6-2 show a very narrow spread of tensile strength value whatever the processing parameters. The combined results of all the experiments produced a tensile spread of only 24-27.5 MPa which is not significant given no apparent trends related to parameters exist in terms of this spread.

The lack of parameter effects on polypropylene mouldings may be due to the inherent properties of polypropylene itself. According to theories on molecular diffusion, polypropylene would have more time to both diffuse and relax across the interface than for example an amorphous material such as polystyrene at the same temperature [Painter,1997]. The result would be good global load sharing across the bulk of the moulding for strength measurements. This is the result of a low glass transition temperature (T_g) of -20°C compared to a T_g of 90°C for polystyrene. The PP would stay mobile for much longer than the polystyrene. Of course this simple analogy is complicated by the onset of crystal formation in the polypropylene samples which would make diffusion difficult. But, this would also suggest, that if these experiments had been repeated using another material such as polystyrene, a pattern of processing parameter effects may have been visible. For example the use of higher than standard temperatures would retard the onset of T_g in the core allowing greater diffusion and a possible improvement in the properties of polystyrene co-injection mouldings compared to those moulded at lower temperatures. Attempts to perform these experiments were unsuccessful as the tooling used for these experiments was designed for polypropylene which shrinks substantially more in the tool than polystyrene. Therefore, in order to do these experiments, modifications, specifically to increase the draft angle on the cavity would have been required.

Since the effects of packing parameters appeared minor for all three properties it was decided that it was unnecessary to evaluate these effects on the co-injection moulded specimens.

6.1.2 Tensile Modulus and Elongation

Processing property effects could be seen for changes in melt temperature and injection speed and less so in mould temperature. These results can be seen in Tables 5-6 to 5-8 and 5-14 to 5-16. In general as melt temperature, mould temperature and injection speed increase, modulus goes down and elongation goes up. This appears to be true for both injection and co-injection mouldings. The co-injection mouldings also appear to have a higher modulus and lower elongation than standard injection mouldings. This trend for modulus is shown in Figure 6-3. This implies that somewhere in the process there is difference in the moulding regime and that mouldings produced by co-injection moulding are undergoing a different and hitherto unreported mechanism.

One possible explanation for this difference could be a varying thickness in the orientated skin layer of the mouldings. It would be expected that a deeper skin layer would produce a higher tensile modulus and a lower elongation. Faster core injection speeds are known to reduce the thickness of the skin layer in the gate region. This is due to shear heating and remelting in co-injection moulding, removing skin layers into the molten flow [Rungseesantivanon, 2000]. This would lead to less orientation of the moulding as a whole, as a consequence of a reduced skin layer. This would then lower modulus and increase elongation. Melt and mould temperatures would again affect the skin layer formation. The reduced effect of mould temperature in

these experiments could be attributed to the fairly limited range of temperatures assessed here, due to the limitations of the equipment, further effects may have been seen if mould temperatures had been further increased.

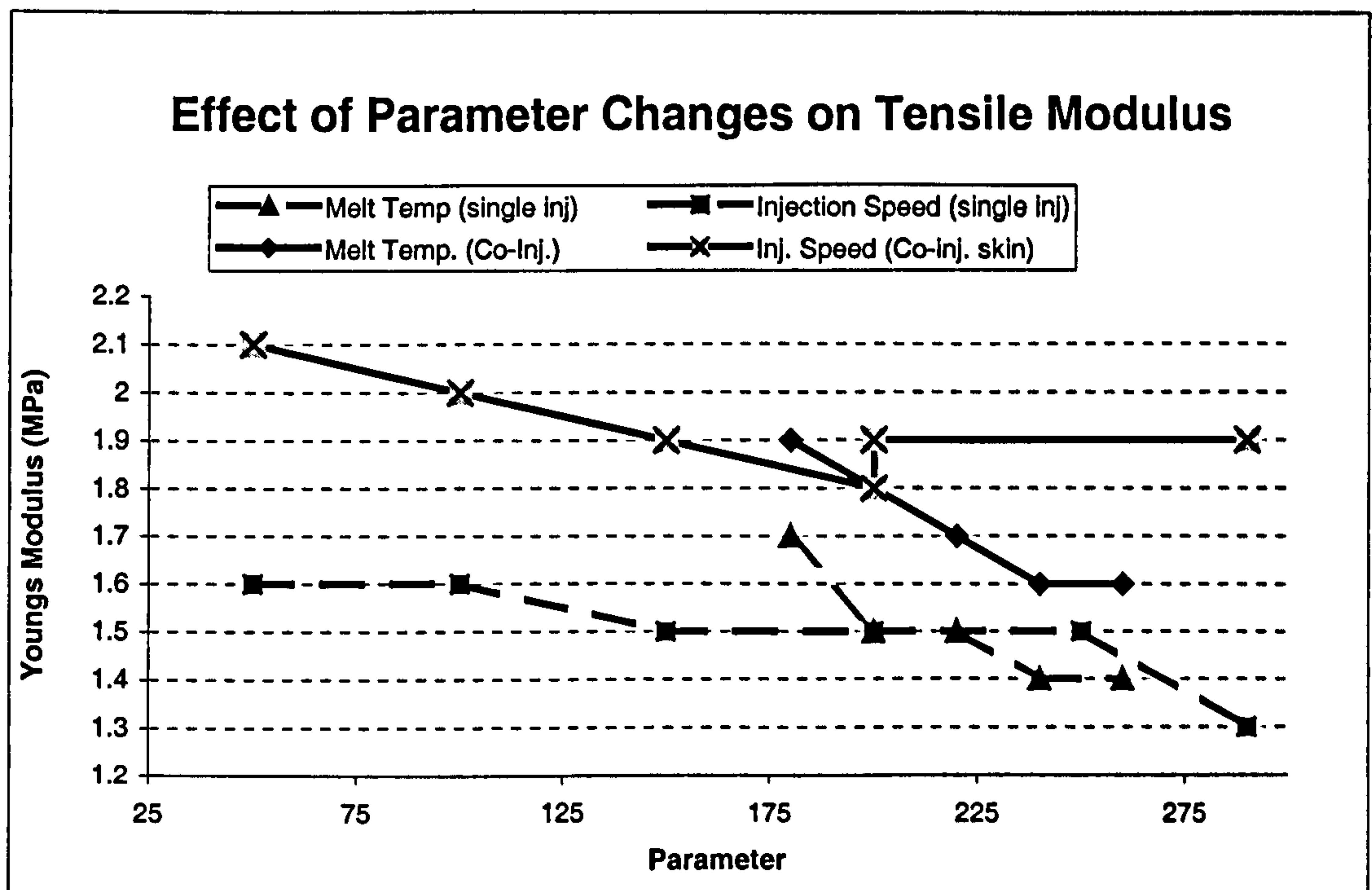


Figure 6-3 Effect of Injection Speed and Melt Temperature on Modulus

The increased modulus and reduced elongation of the co-injection mouldings compared to the standard mouldings suggest that co-injection mouldings on average, produce a thicker orientated skin layer than standard injection mouldings (as was shown in Figure 2-2). Therefore, compared to standard injection moulding this offers the opportunity to selectively enhance molecular orientation and therefore modulus properties. Another technology exists that also applies controlled orientation in injection moulding, shear-controlled orientation in injection moulding (SCORIM) [Kalay, 1997]. This requires a device fitted on the nozzle of the machine and produces a shish-kebab

morphology in the shear influenced region. This process results in substantial improvements in polypropylene mechanical properties and it is likely combining technologies such as co-injection moulding and SCORIM will present further opportunities in this field.

In relation to these experiments, if it is considered that the injection of the core material is delayed 0.1s, any shear heating and remelting of skin material would be increased relative to the same position, at the same injection speed. Figure 2-5 illustrated the effects on cavity pressure and screw movement using two types of multi-injection, diagrams such as these highlight that differences are occurring. It is possible to envisage such a diagram to demonstrate the differences of other parameters such as shear heating between injection moulding and co-injection moulding assuming the same skin and core velocity such as shown in Figure 6-4.

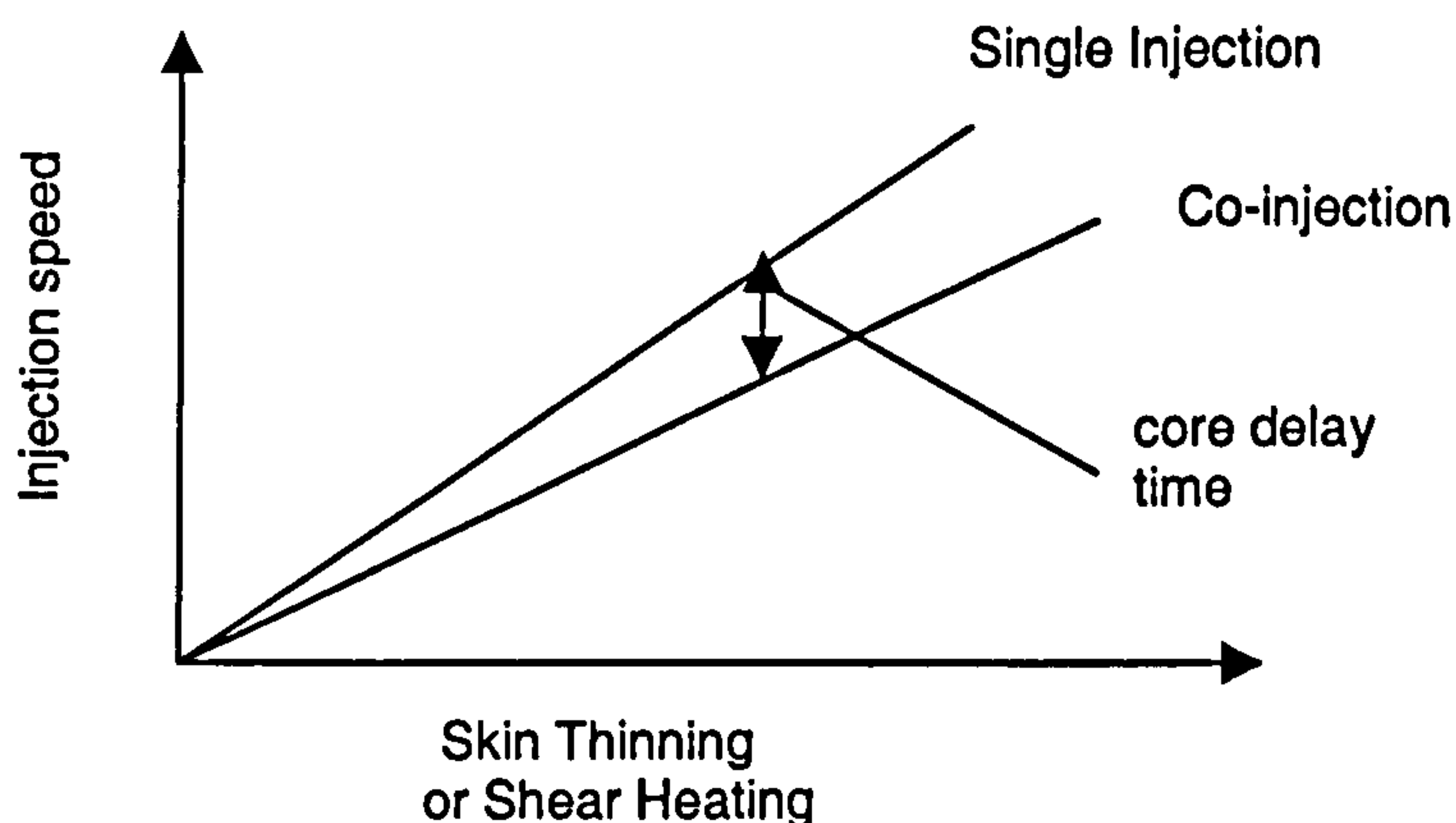


Figure 6-4 Difference in Skin Thinning between Single injection and Co-injection

However as well as the delay on the core, co-injection moulding also enables skin and core to be injected at different speeds. This effect can perhaps best

be explained by considering two co-injection moulded specimens whose core was injected with a 0.1sec delay but with two different core speeds whilst the skin speed was kept constant. The results in Table 6-1 are reproduced from Table 5-16.

Injection Speed	200	200
Skin		
Injection Speed	150	25
Core		
<i>Tensile Strength (MPa)</i>	27.0	26.5
<i>Tensile Modulus(GPa)</i>	1.8	1.9
<i>Elongation (%)</i>	40.9	48.4

Table 6-1 Effect of core speed on properties

Table 6-1 shows with a higher core injection speed both modulus and elongation are reduced relative to their values when a much slower core speed is used. This seems at odds to previous findings here and suggests that it is not only the injection speed of the core layer that affects skin layer formation but also that the relative speed of skin to core formation is of utmost importance in property/parameter relationships. This is further supported by the trend seen in Figure 6-5.

Here it appears that increasing the difference in the relative speeds tends to increase the elongation, this would suggest a mechanism as shown in Figure 6-6 whereby the difference in the relative speeds of skin and core causes a change in shear regime. At lower relative core speeds there is less shear and hence lower levels of orientation giving higher elongation properties in the mouldings.

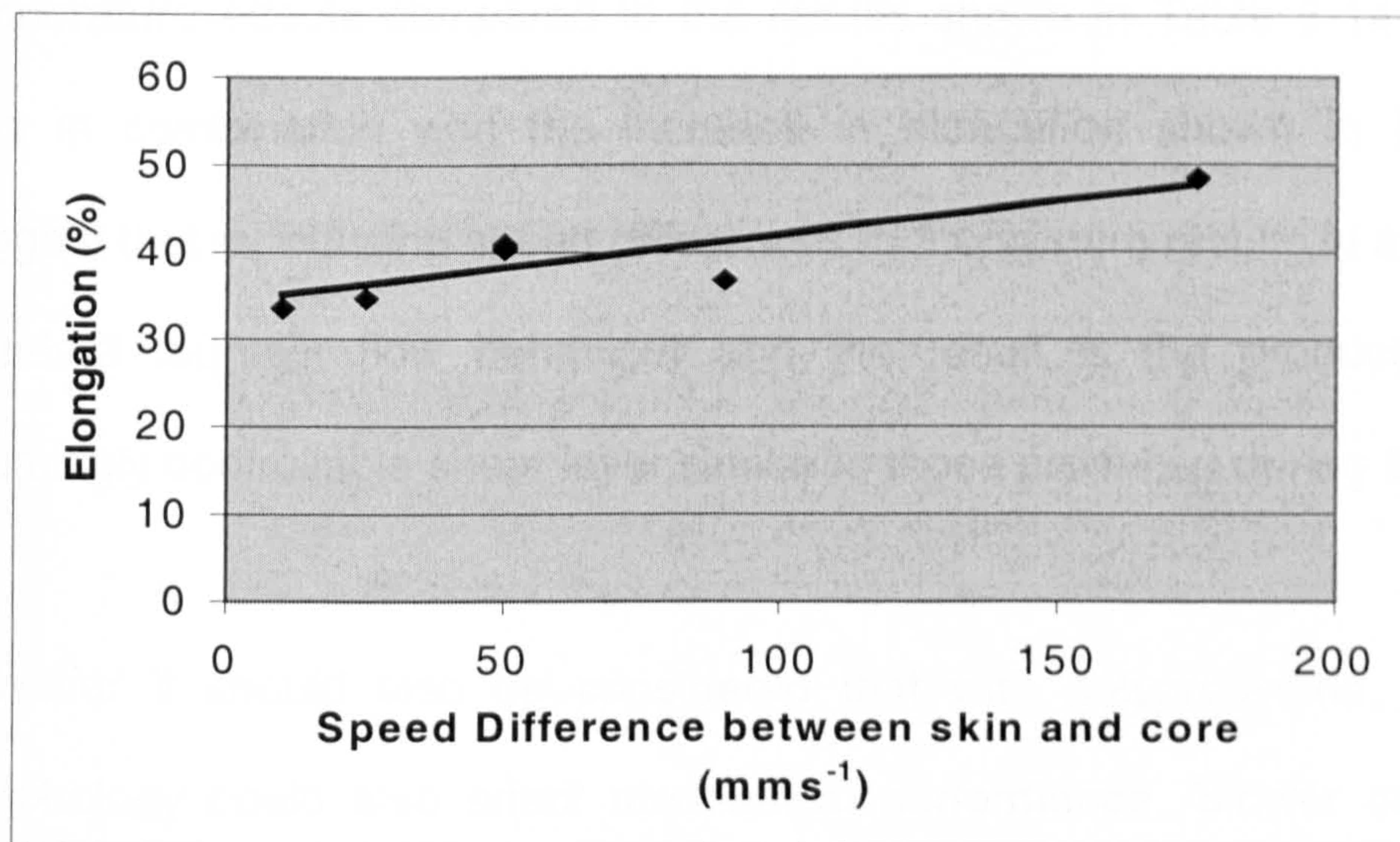


Figure 6-5 Effect of the difference in skin and core injection speeds on elongation

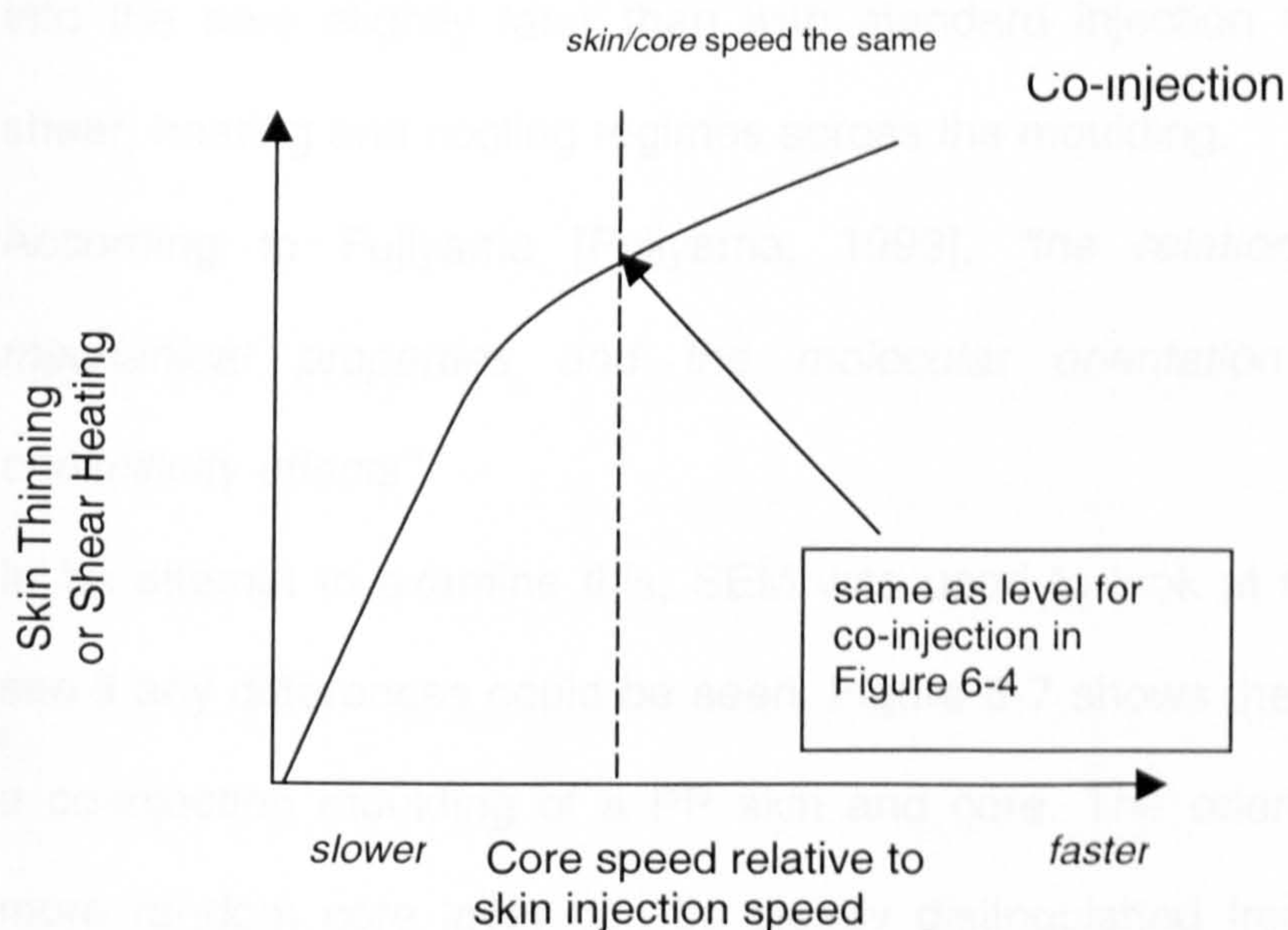


Figure 6-6 Effect of core speed relative to skin speed on skin thickness

Introducing a difference between the speeds of the skin and core (Table 5-16) appears to enhance both modulus and elongation properties relative to temperature effects compared to the results shown in Table 5-14 and 5-15. This in combination with the increase in elongation shown in Figure 6-5 suggest that introducing speed differences in the system results in a change to standard fountain flow behaviour and the result is the production of a seemingly controllable shear layer similar to those produced during SCORIM.

However it should also be considered that with polypropylene, crystalline morphology could also affect mechanical performance. Slower cooling can induce higher crystallinity and an increase in modulus, this could also be a factor in the improvement of modulus relative to standard injection for the co-injection moulded samples. The delay on the core, would put molten material into the core slightly later than with standard injection mouldings affecting shear, heating and cooling regimes across the moulding.

According to Fujiyama [Fujiyama, 1999], *"the relationship between the mechanical properties and the molecular orientation is 'smeared' by crystallinity effects"*.

In an attempt to examine this, SEM was used to look at fracture surfaces to see if any differences could be seen. Figure 6-7 shows the fracture surface of a co-injection moulding of a PP skin and core. The orientated skin and the more random core layer can be clearly distinguished from each other. The tendrils are a result of the deformation and fracture mechanism taking place during tensile testing. They appear to link the skin and core layers, suggesting

good adhesion is occurring at the boundary as would be expected in a system of compatible materials. This could explain why the strength of the polypropylene appears constant whatever the processing conditions and implies that in terms of tensile strength, this bonding occurring naturally by diffusion and relaxation may be the major determinants.

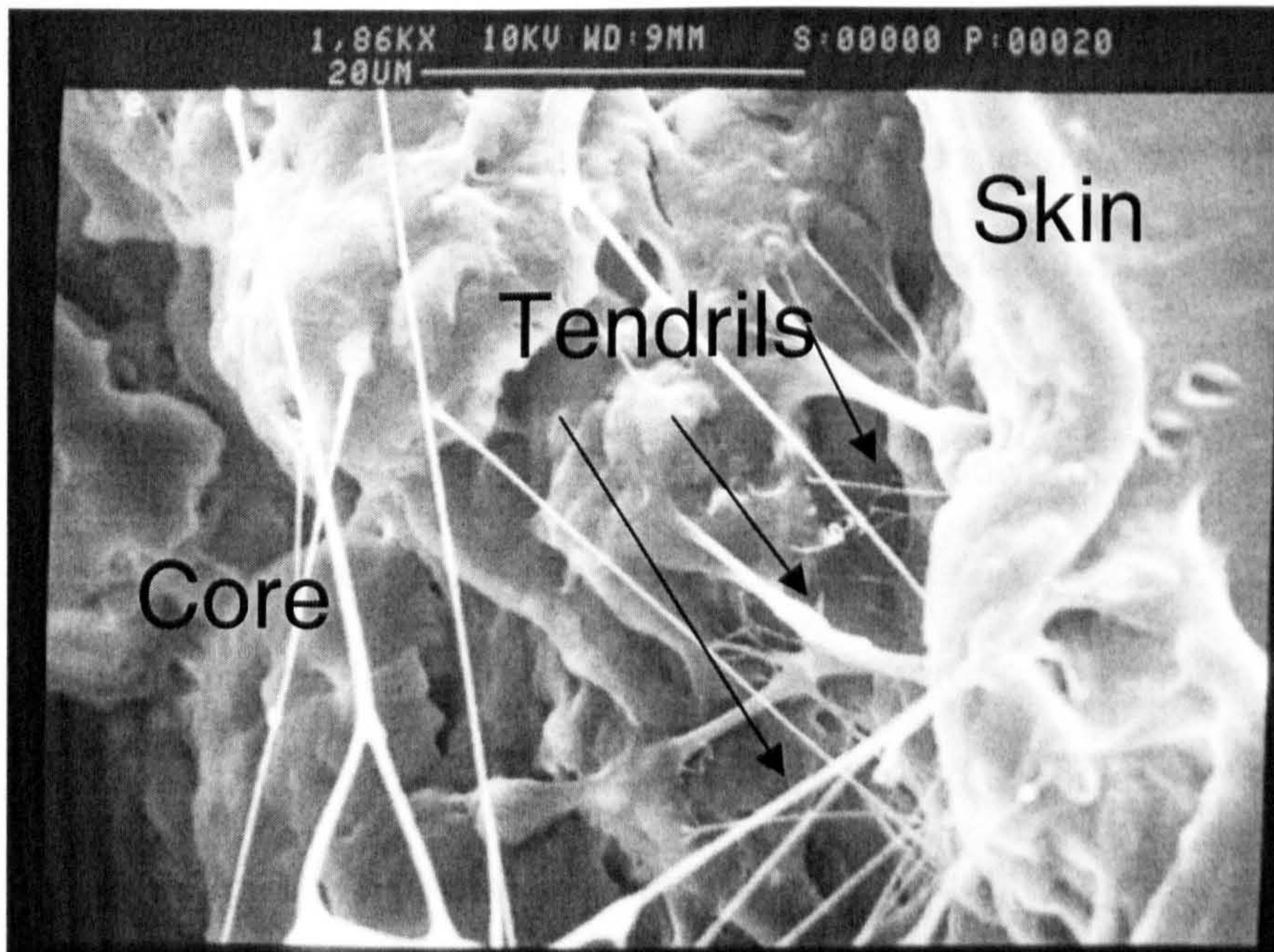


Figure 6-7 Co-injection moulding of PP skin and PP core

Figure 6-8 appears to show the effects of shear heating on standard injection moulding specimens. Debris that has been remelted and encapsulated can be clearly seen in this sample indicating that material is being deposited and then a mechanism of shear remelting is occurring with incoming molten flow. This moulding was produced using a high injection speed and could support the argument that skin/core formation can be affected by re-depositing of skin material due to shear heating as illustrated in Figure 6-6. However, it can equally be argued that due to the deformation that has taken place during

testing of the sample and the fact that these debris do not show this deformation, these less deformed materials could be a result of contamination of specimens during preparation. SEM provides a qualitative and therefore subjective method of analysis, often open to differing interpretation.

It is also interesting to compare Figure 6-8 with Figure 6-9. The scaling of both pictures is similar, however the structure appears quite different. Core material on the left of Figure 6-9 seems to have a much coarser morphology than that shown in Figure 6-8 which would support the earlier supposition that a different cooling regime and crystal formation is taking place. In Figure 6-8 the stretching deformation and elongation of the polypropylene can be seen. In Figure 6-9 where failure was more brittle, the interface looks sharper. This visualisation reinforces the results and differences seen in the elongation properties and suggests they are strongly linked to molecular structure. Figure 6-9 also appears to show two differing behaviours from the skin and main body of the moulding, as if the skin has cracked before the core. This could suggest failure of adhesion between the skin and core boundary layer.

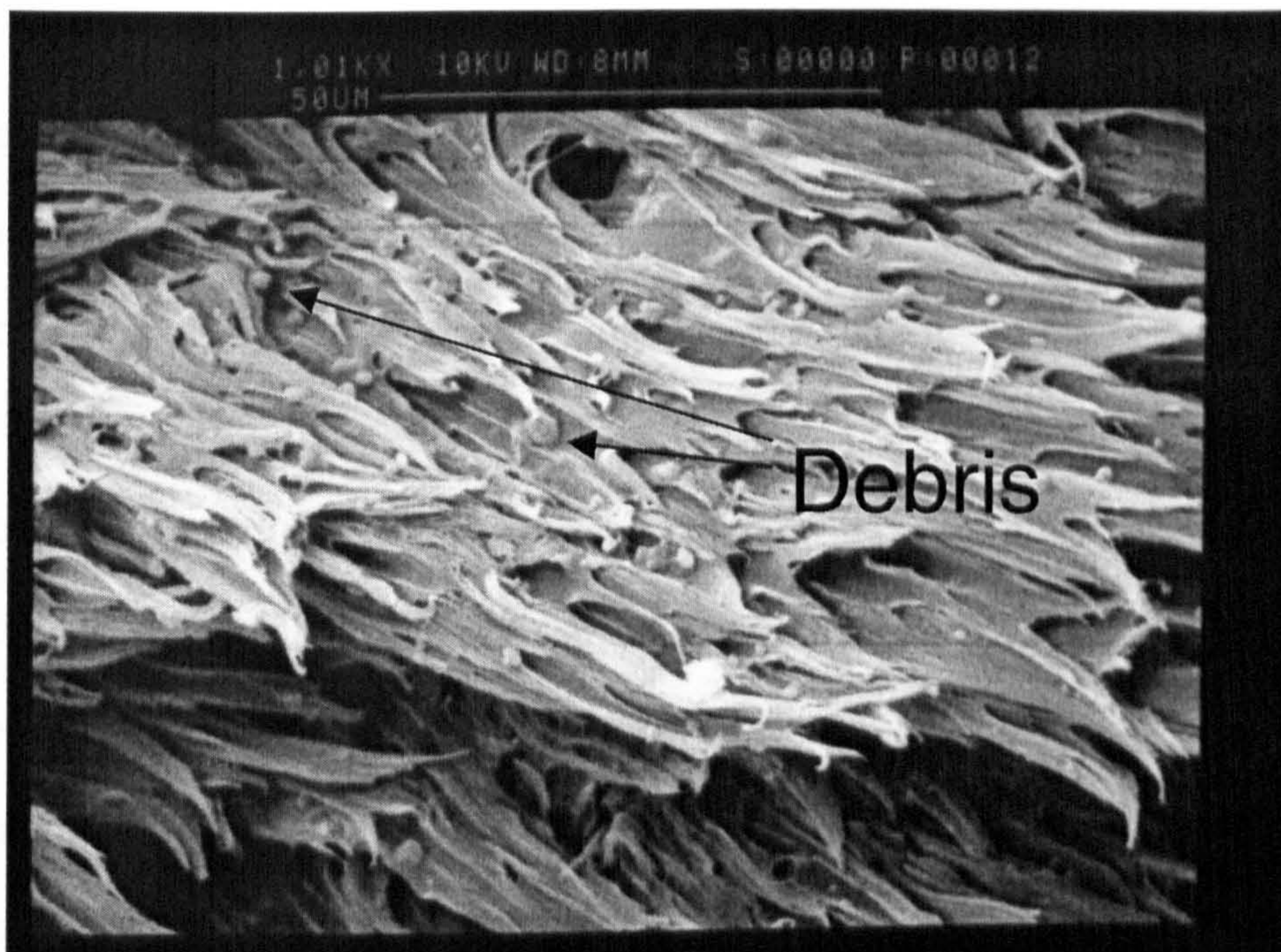


Figure 6-8 SEM of standard injection moulded polypropylene, (injection speed $290\text{mm}^{-1}\text{s}$)

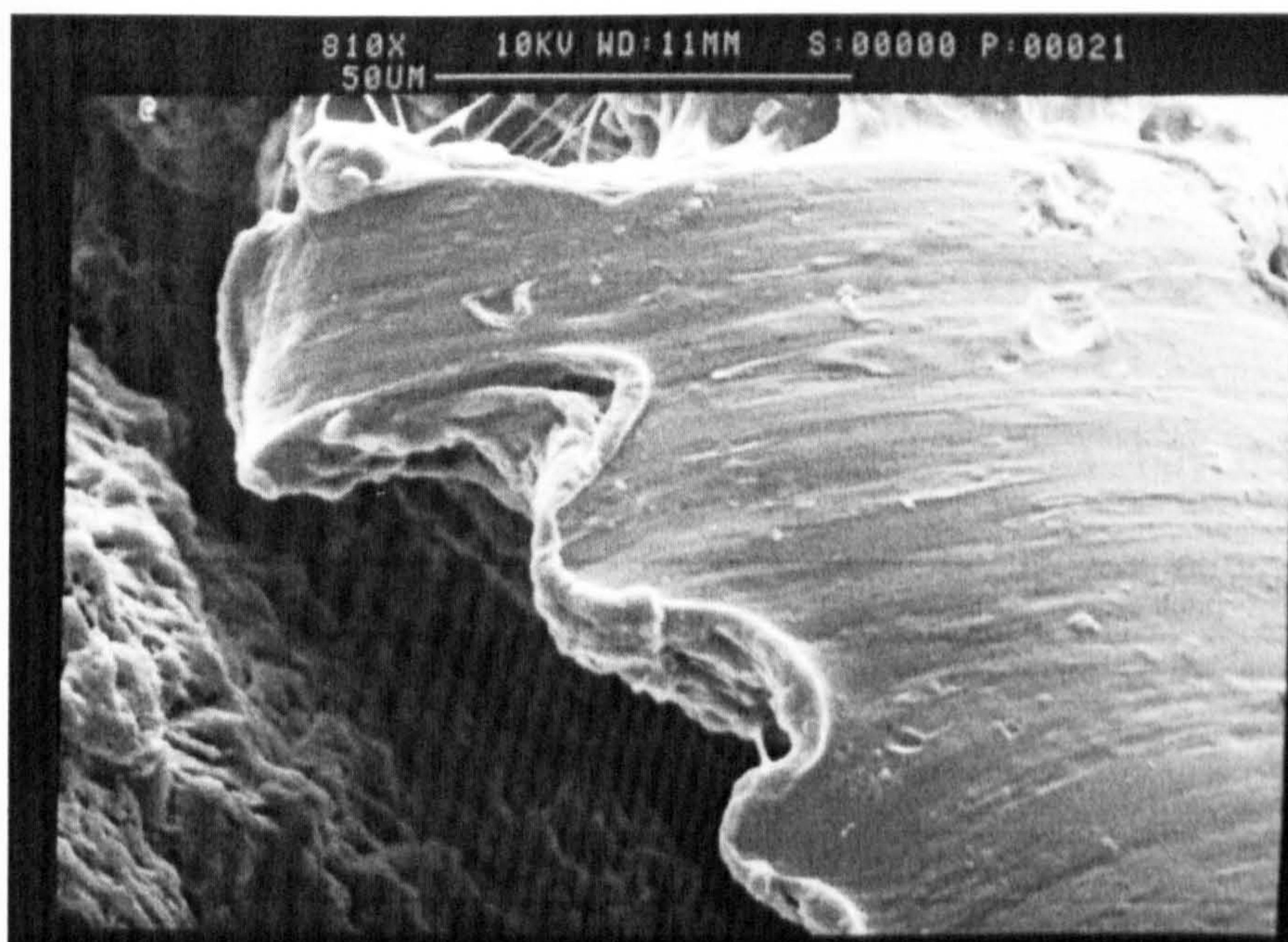


Figure 6-9 Co-injection moulding fracture surface of PP skin and PP core

From these limited studies it can be argued that diffusion and relaxation are likely to be the driving mechanisms for the strength of the PP skin/PP core mouldings and these mechanisms occur at speeds fast enough not to be affected by changes in moulding parameters. In contrast, modulus and elongation are dependent on the thickness of the orientated skin layer and the morphology development. Whilst this appears to be an original finding, it is clear that much further work in this area is required to further examine these relationships and how they would change using other material combinations. In terms of this research, the importance of diffusion, orientation and morphology in co-injection moulding and their relation to moulding parameters has been shown.

6.2 *Parameter effects as a result of viscosity differences*

Consideration can now be given to what changes may occur if viscosity differences exist in the skin and core components. For example, consider a system with a PP skin and core, where the viscosities of the two materials are very similar. The gradients in pressure and temperature will be fairly constant at the interface. Injection speeds will be similar and the simultaneous phase will produce a period whereby the two layers can interact in terms of stress relaxation and interdiffusion.

Now consider a system where the core viscosity is much higher than the skin. The injection speed of the core will be increased to improve core distribution and a gradient at the interface will be created in terms of stress, pressure and temperature. The period of simultaneous injection will by default become less, allowing less time for any dissipation of stresses in the form of molecular relaxation by diffusion across the interface as shown in Figure 6-11.

In the reverse scenario the core viscosity is much lower than the skin. The core must be delayed to prevent it flowing through the skin through areas of lower pressure creating melt fingering as predicted by rheological theory [Cogswell, 1996]. Again the changes in the machine set-up to injection speed, delay and simultaneous phase set up gradients across the interface of the moulding and again the period of simultaneous injection is reduced.

The pressure gradient is a result of viscosity changes occurring in the system. Higher viscosities materials require higher injection pressures. A system consisting of a core material of higher viscosity will therefore require a higher pressure when the more flow resistant core material is injected, likewise when core flow stops, the system will require less pressure. A gradient will exist at both the point of switchover to the simultaneous phase and the point at which core flow stops. A pressure gradient will therefore exist at the flowfront. This is illustrated in Figure 6-10, with regard to the three possible viscosity combinations.

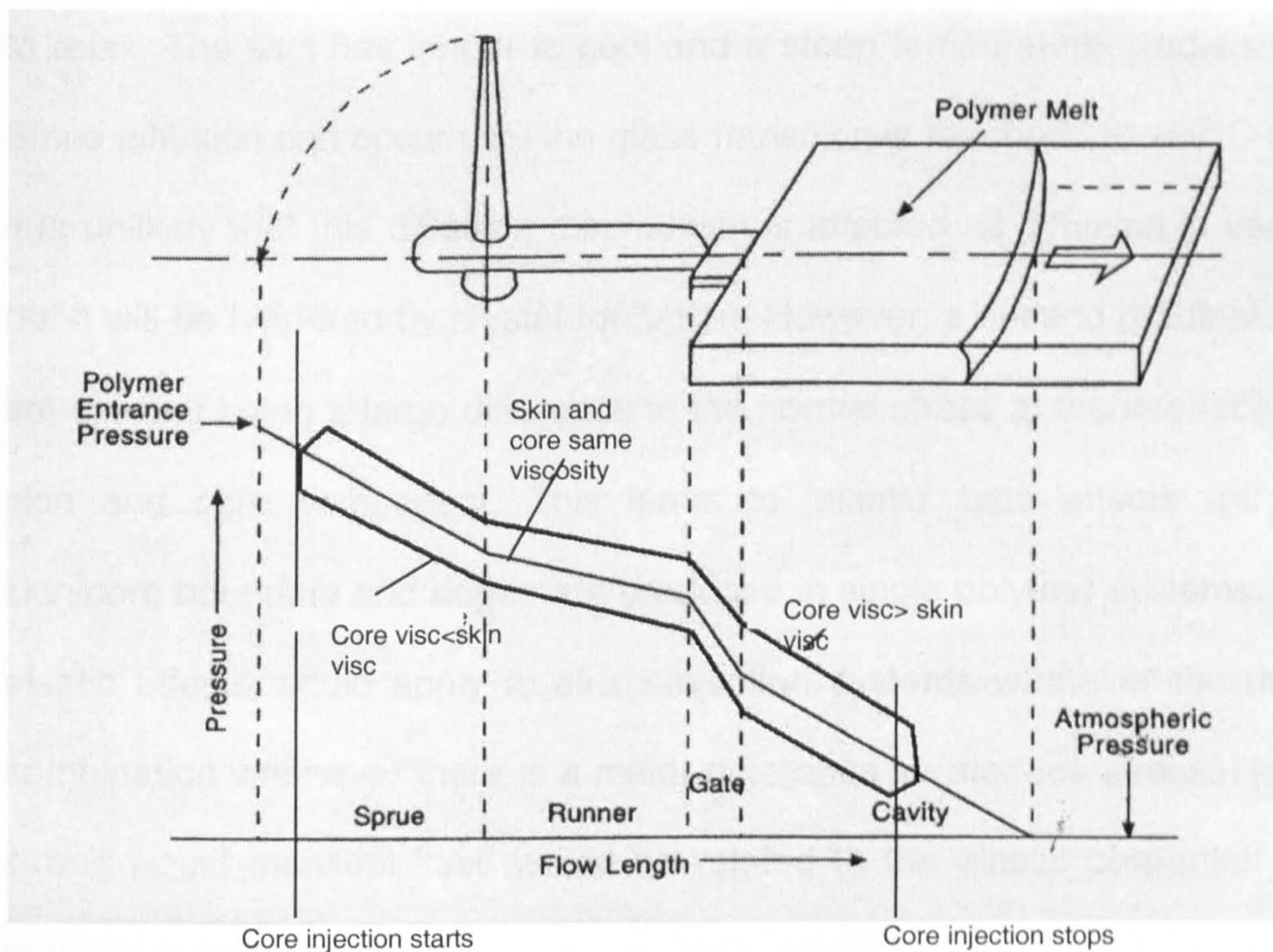


Figure 6-10 Pressure Variations as a result of viscosity changes

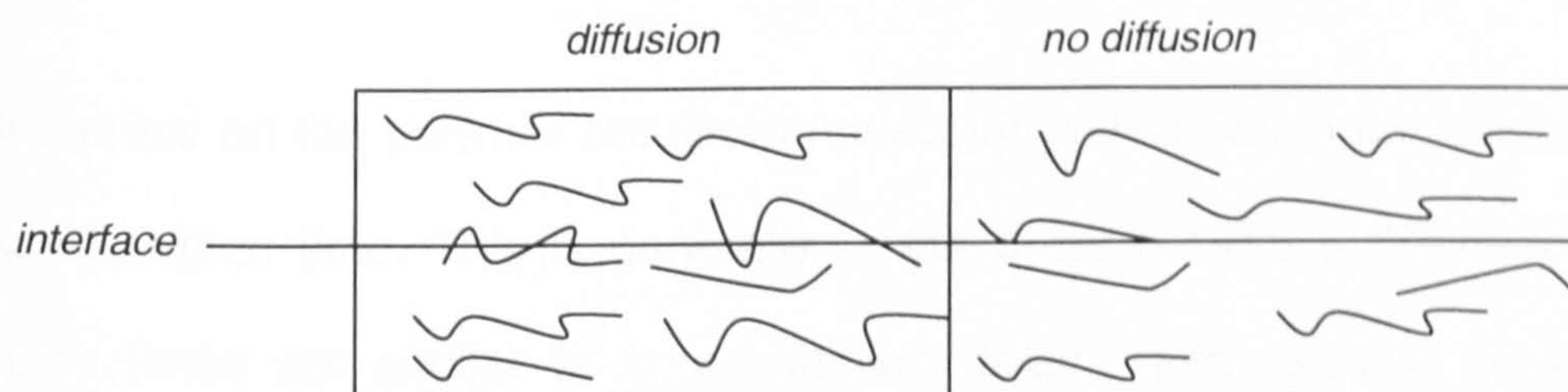


Figure 6-11 Molecular diffusion across the interface (left) and none (right)

As there can be diffusion and stress relaxation across this interface in a PP system, much of the stress can be dissipated across it. However as seen in scoping experiments, if mouldings are produced in such a way to inhibit the diffusion and relaxation mechanisms, ridges can be produced in single polymer

systems. This is achieved by using a delay on core injection and then a very high core injection speed. The core is subject to increased stress with less time to relax. The skin has longer to cool and a steep temperature gradient exists. Since diffusion can occur until the glass transition is reached i.e. -20°C for PP, it is unlikely that this diffusion mechanism is affected as diffusion is very fast, but it will be hindered by crystal formation. However, a second gradient is also set-up, that being a large difference in the normal stress at the interface of the skin and core component. This leads to 'elastic' type effects within the skin/core boundary and ridges are produced in single polymer systems. These elastic effects would apply to all co-injection systems whatever the material combination whenever there is a major difference in interface stress. How this stress would manifest itself would be related to the elastic properties of the material in question.

6.3 *The Effects of Stress on Polymer Melts*

The stress on the polymer results in molecular coiling which can be given by the relaxation time. This is generally in the order 0.1-0.5 s [Brydson,1981]. These times are similar to core injection delay times used in co-injection moulding which are also generally in the order 0.1-0.5 s. This means relaxation of the skin may already have occurred when the core component is injected. The amount of coiling (orientation) will be related to the amount of shear, increasing at higher rates. These rates will be greatest at the wall of the tool (or at an immiscible polymer-polymer interface). Orientation is maintained for as long as the melt is in motion or unless slip-stick mechanisms such as those noted in Chapter Four by Hobbs [Hobbs, 1996] occur. Once filling is complete

the shearing forces are released and the molecules can begin to re-coil until the melt solidifies, causing any remaining orientation to be frozen in. The result of this is effects such as the 'halo' effect as seen in the mouldings of PA12/PP reported by Goodship and Kirwan [Goodship, 2001, a] and shown in Figure 2-8. Effects such as these can have a detrimental effect on moulding appearance and although undetermined at this time, it is reasonable to assume will be detrimental to physical properties also. According to Brydson [Brydson,1981], the level of this orientation will depend on :

- the initial levels of orientation, caused by exposure to shear
- average relaxation time of the polymer in the processing range to solidifying
- time available: function of size and shape of moulding, its specific heat, the magnitude of the difference between processing temperature and solidifying temperature and the mould temperature.

It is these points that are likely to be key to the ridge creation. A high core injection speed will induce more shear and therefore stress and orientation. Delaying injection of the core will reduce the relaxation time available and the skin will already have begun to cool. However, because the polymer has been exposed to higher levels of stress, the relaxation time required will actually have increased.

Given that instabilities can exist regardless of the polymer type, it is not surprising that one exists in the PA6/ PP system that was the initial subject of this study.

6.3.1 Mixed-Polymer Systems

In the case of polymers with different processing temperature ranges there is the added complication of a mismatch in temperatures automatically creating an even steeper and uneven temperature gradient at the interface. For example with a Nylon/ PP system: The nylon is less viscous, the PP more viscous. The injection speed of the PP must be higher to get good distribution. This also sets up a pressure gradient at the interface. When the flow fronts meet their immiscible nature means that built in stresses such as these cannot be released by the mechanism shown in Figure 6-10. When the component is in the mould, the geometry will be constrained by contact at the mould surface. When it is released, the viscoelastic nature of plastics means they will try to return to the state of having only internal isotropic stresses. Therefore in regions of highest stress concentration, the stresses will try to dissipate. The result is a ridge.

According to Rungseesantivanon [Rungseesantivanon, 2000] there is no software mould prediction packages for simultaneous co-injection moulding, however, there are systems for sequential co-injection moulding. In applying these packages to mixed material mouldings (or in some cases single polymer systems) there are problems. They assume a steady state at the interface, free from pressure or temperature gradients and this work has shown they are fundamentally flawed in design. In general, the interface is a region of variance and non-equilibrium conditions.

In considering the mechanisms underlying the ridge effect, it appears that a number of factors are implicated. Firstly viscosity, since matched viscosities

and materials would present a fairly steady interface in terms of temperature, speed and stress.

Work by other researchers in the field of mould filling and simulation [Somnuk, 1995], [Young, 1980] have considered viscosity ratio to be the major factor in skin / core distribution and on first examination this also appears to be a driving factor in the formation of ridge effects. A mismatch in viscosity ratio leads to a surface distortion when mouldings are produced such as in PA6 and PA12 skin and PP core mouldings. However, since ridge effects can be induced when the skin/core materials and viscosities are the same, as seen in the preliminary moulding trials on PP, it appears that it is not only differences in viscosity causing the ridge.

It is also worth noting here, that instabilities are reported in co-extrusion of systems consisting of the same material [Michaeli,1992]. This also supports the case that a viscosity mismatch alone is not the cause of the ridge effect. Changes in certain parameters, in this case high core injection speeds and a core injection delay, also produce the ridge and suggest that with these parameters an unsteady interface is produced. It may be argued that the effect of shear on viscosity, i.e. higher shear producing a lowering of viscosity, could be the cause of the ridge.

It is therefore postulated that the ridge could be due to two possible causes:

- The result of the processing parameters, which have to be used to distribute materials with mismatched viscosities.
- The effects of shear on viscosity ratios.

The next sets of experiments use immiscible systems to further examine these effects.

Chapter 7. Mixed Polymer Systems

This chapter builds on the findings discussed in Chapter 6 by examining immiscible systems. It looks to elaborate on the following areas.

- Identifying mechanisms of surface distortion
- Determine process conditions to minimise surface distortions

7.1 *Diffusion and relaxation*

It has been shown that diffusion and relaxation appear to play a major part in dissipating stress across the interface. Therefore the next set of experiments were planned to explore the circumstances where there could be only limited or no diffusion and relaxation taking place across the skin and core. For this compatibilised systems of PP and PA6 were used with a compatibiliser to bond the immiscible skin and core at the interface. This mimics the work of Selden [Selden 1998] and Rungseesantivanon [Rungseesantivanon, 2000] who had both studied this system previously. However, neither had looked at instabilities or tensile properties. A component of diffusion was also introduced into these experiments by examining mouldings with weld-lines and without. Weld-lines are formed when molten flow fronts meet, the extent that they are able to re-combine will determine the associated mechanical property reduction at the weld-

line. It was hoped that these experiments would further highlight the importance of diffusion and relaxation in stress dissipation, as well as giving an indication as to the relative strength of the compatibilised bond.

7.2 *Tensile properties of compatibilised systems with and without weld-lines*

Tooling was required that allowed production of the same components with and without weld-lines. This allowed properties to be readily compared. Tensile analysis was chosen for these experiments for reasons already detailed in section 5.2.1. Sample mouldings are illustrated in Figure 7-1; this also shows both the position of the insert and the position of sampling from the mouldings for tensile tests. Specimens were milled to size and tested as detailed in 5.2.2.

The tool has the dimensions 150 x 150 x 3mm, the hinge cut out is placed 25mm from the gate.

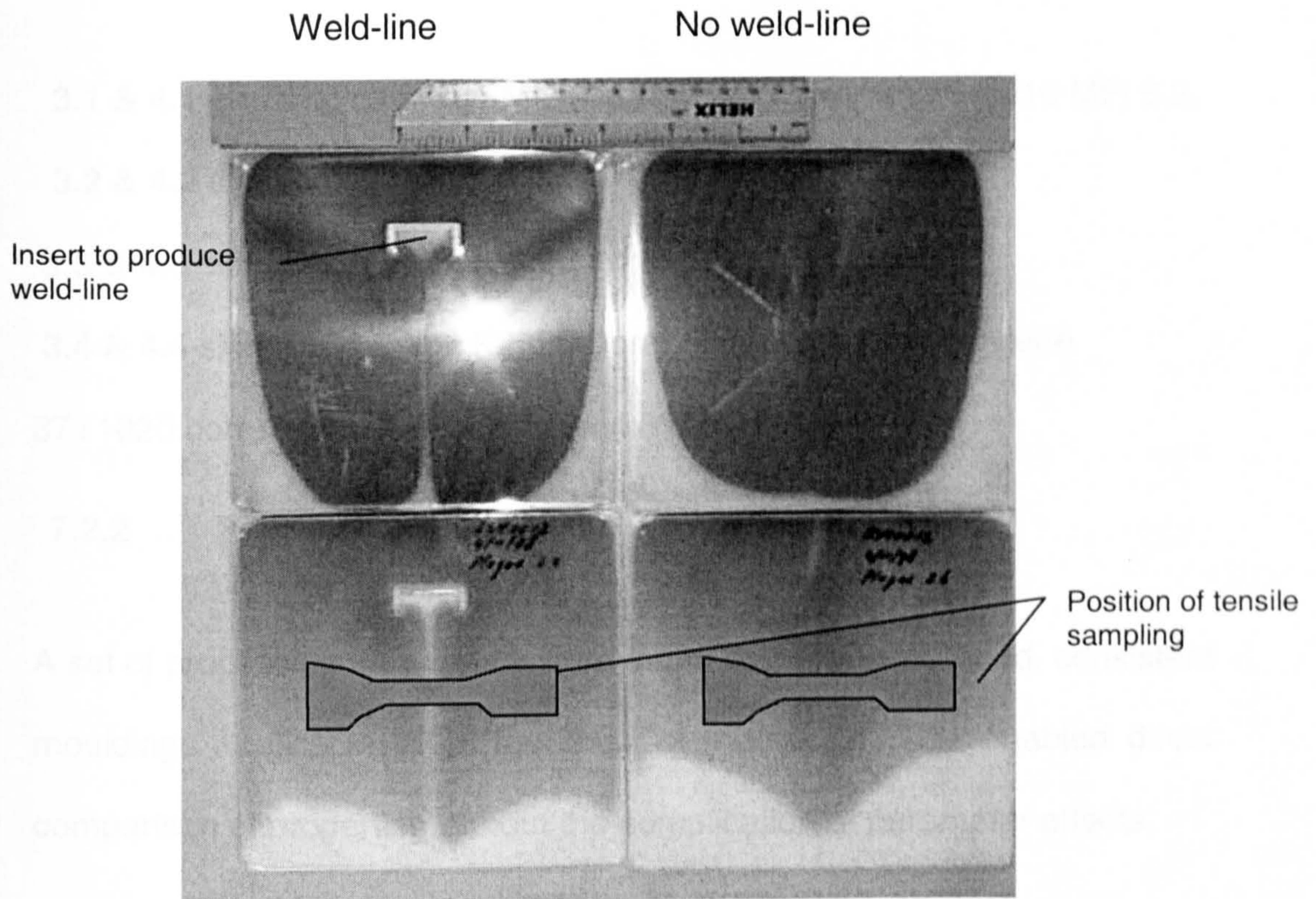


Figure 7-1 Sample mouldings with and without weld-lines

7.2.1 Materials

Four material combinations were chosen. A PP/PP system as used in previous experiments. A 20% talc filled PP as both skin and core and an unfilled grade of nylon 6 as both skin and core. These mouldings act as datums. The fourth system is the compatibilised system of nylon 6 and 20% talc filled PP, doped with 15% compatibiliser as used by previous researchers [Selden, 1998], [Rungseesantivanon, 2000]. The materials and testing codes are shown below, a 3 signifies no weld-line (tests 3.1-

3.4), a 4 signifies a weld-line (tests 4.1-4.4). Samples were produced using a skin/core ratio of 2:1.

3.1 & 4.1 skin and core : DSM polypropylene stamylan P56M10 MFI 6.2.

3.2 & 4.2 skin and core: DSM polypropylene 37T1020 core

3.3 & 4.3 skin: DSM Nylon K222D core: DSM Nylon K222D

3.4 & 4.4 skin: DSM Nylon K222D core: 85% DSM polypropylene 37T1020 core,15% Uniroyal polybond 3150 (dryblended)

7.2.2 Processing Parameters

A set of processing parameters were found that produced good, consistent mouldings applicable to all four sets of mouldings. This enabled direct comparison of properties without the complication of parameter effects.

Parameter	3.1, 4.1	3.2, 4.2	3.3, 4.3	3.4, 4.4
Melt Temperature Barrel A (°C)	250	250	250	250
Melt Temperature Barrel B (°C)	250	250	250	250
Mould Temperature (°C)	60	60	60	60
Injection Speed Barrel A & B (mms⁻¹)	100	100	100	100
Holding pressure (on B) (bar)	50	50	50	50
Set point (mm)	20	20	20	20
Holding time (sec)	15	15	15	15
Cooling time (sec)	40	40	40	40
Metering stroke Barrel A (mm)	84.5	84.0	83.5	83.5
Metering stroke Barrel B (mm)	41	40	39	41
Injection delay on B (sec)	0.1	0.1	0.1	0.1
Back pressure A & B (bar)	5	5	5	5

Table 7-1 Processing conditions for Experiments 3 & 4

7.2.3 Experimental Procedure

The materials for experiments 3.3/4.3 and 3.4/4.4 were predried before moulding for 4 hours at 80°C. This is because both the nylon and the compatibiliser are hygroscopic.

The mouldings were produced as shown in Table 7-1. The first five mouldings produced were discarded in each case while steady state conditions were reached. At least ten samples were produced of each moulding with five randomly selected for tensile testing. This meant samples were available if further tensile testing was required.

7.2.4 Result Summary

7.2.4.1. Test 1 PP datum.

	No weld – line Test 3.1	weld-line Test 4.1	% property reduction
<i>Tensile Strength (MPa)</i>	30.22	26.75	11.5
<i>Young's Modulus (GPa)</i>	1.8	1.6	11.1
<i>Elongation (%)</i>	32.69	11.59	64.5

Table 7-2 Comparison of unfilled polypropylene co-injection moulding, with and without weld-line

7.2.4.2. Test 2: 20% Talc filled PP datum

	No weld – line Test 3.2	weld-line Test 4.2	% property reduction
<i>Tensile Strength (MPa)</i>	32.1	28.4	11.5
<i>Young's Modulus (GPa)</i>	2.4	2.1	12.5
<i>Elongation (%)</i>	15.8	7.6	51.9

Table 7-3 Comparison of 20% talc filled polypropylene co-injection moulding, with and without weld-line

7.2.4.3. Test 3: Nylon 6 datum

	No weld – line Test 3.3	weld-line Test 4.3	% property reduction
<i>Tensile Strength (MPa)</i>	53.2	45.3	14.8
<i>Young's Modulus (GPa)</i>	1.8	1.6	11.1
<i>Elongation (%)</i>	75	53.2	46.4

Table 7-4 Comparison of nylon 6 co-injection moulding, with and without weld-line

7.2.4.4. Test 4: Nylon 6 skin/ 20% talc PP Core

	No weld – line Test 3.4	weld-line Test 4.4	% property reduction
<i>Tensile Strength (MPa)</i>	23.3	23.6	- 1.3
<i>Young's Modulus (GPa)</i>	1.2	0.8	25.0
<i>Elongation (%)</i>	15.8	11.2	64.9

Table 7-5 Comparison of Nylon 6 skin/PP core co-injection moulding, with and without weld-line

7.2.5 Discussion of Tensile Properties

In the single polymer systems, tensile behaviour was as expected for both weld and non-weld-line samples and tensile failure took place at the weld-line. These tensile results (see Table 7-2 to 7-4) reflect a reduction in properties as a result of the failure of the materials to fully recombine. This is a well known problem with weld-lines [Liu, 2000].

With the compatibilised system (Table 7-5), tensile failure did not take place at the weld-line but at the skin/core interface. So even when a potential weakness in the shape of a weld-line was introduced (which in the case of co-injection mouldings consists of 100% skin), failure still took place at the compatibilised interface. This suggests the strength of the compatibilised bond that is produced is relatively weak, a finding not recognised by either Selden [Selden, 1998] or Rungseesantivanon [Rungseesantivanon, 2000] in their peel test experiments. This is believed to be a novel finding. The results from Table 7-5 are also interesting in terms of the property reduction in modulus and elongation measurements caused by the introduction of a weld-line. This might be explained in that the level of adhesion between skin and core in the weld and non-weld line samples varies despite the same compatibiliser content and similar moulding temperatures being applied. Alternatively, it could be that the weld-line is introducing a disruption in the filling pattern of two materials with very different flow characteristics.

Given that both Akay [Akay, 1983] and Selden had highlighted the importance of injection speed, it was decided to further assess this moulding parameter in terms of trying to improve the tensile properties of the compatibilised sample. This was to be achieved by increasing the injection speed to induce the formation of the banded laminate layers observed by these researchers and hence produce a mechanical locking mechanism within the moulding.

7.3 *Effect of injection speed on a Compatibilised Nylon 6/PP system (Experiment 5)*

The tooling, materials and parameters were the same as used for experiments 3.4 in Table 7-1. Four different values of injection speed were used, with the same speed used for both skin and core. The results can be seen in Table 7-6.

Injection Speed Skin and core (mms ⁻¹)	100	150	200	250
Tensile Strength (Mpa)	23.3	23.0	23.6	24.0
Young's Modulus (Gpa)	1.2	1.4	1.4	1.5
Elongation (%)	15.8	15.4	15.0	14.8

Table 7-6 Results of Variation of injection speed for PA6/PP mouldings

7.3.1 Discussion of Results

Interestingly, like the experiments in Chapter 5, strength is not affected but again the pattern of increased modulus and reduced elongation can be seen as the injection speed is increased. As indicated previously, these speed effects were also found by Selden [Selden, 1998] but with regard to peel strength improvements. Since compatibilisation technology relies on the skin/core contact time for chemical adhesion to occur and that this contact time is reduced by increased injection speeds, another mechanism of bond formation is occurring. One possibility was that it was some kind of mechanical interlocking. The increase in modulus could be attributed to these mechanical bonds causing local stiffening effects, similar to a strain hardening effect in metals [Askeland, 1984]. Elongation would be reduced due to the physical effect of these mechanical interlocks on the stretching of the chains. This is illustrated in Figure 7-2, where the physical presence of the mechanical interlocks prevents molecular orientation in the shear direction. It is likely these interlocks will be in the region of 0.1-1mm in size, this size depending on moulding parameters. The basis for this size being in surface profile data which will be discussed in greater depth in later sections.

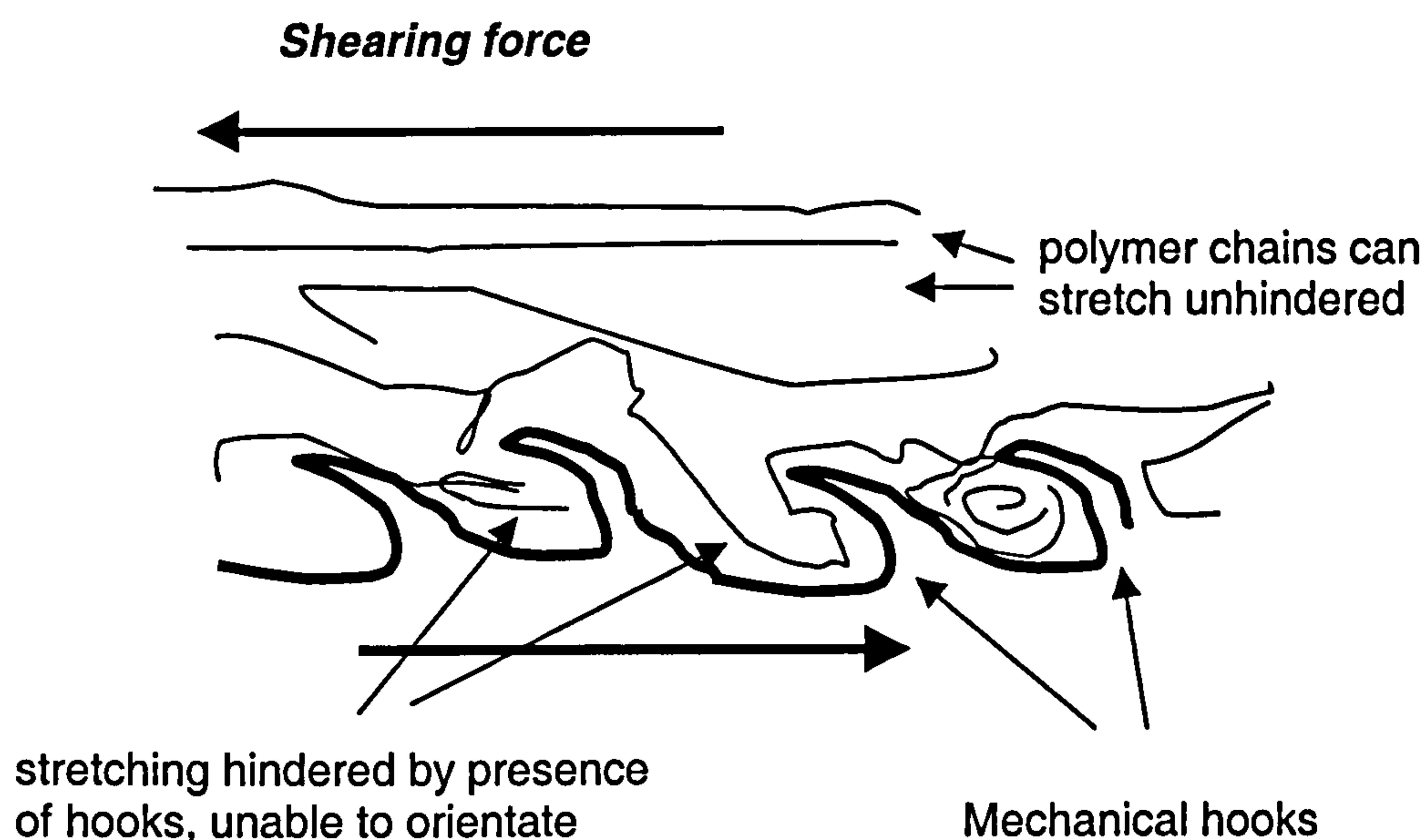


Figure 7-2 Effects of mechanical hooks on molecular orientation

Although mechanical interlocks were not observed at the interface in the PP/PP co-injection mouldings detailed in Chapter 5, these mouldings did show a drop in elongation. It is plausible that such layers would occur in mouldings of the same type of material but these mixing effects would be harder to detect due to the miscible nature of the two components. However the material making up the mechanical interlock would be orientated at different angles to the main body of flow, so elongation properties would be effected. The mechanisms of the interlock will be discussed in more depth in the next chapter.

It is now important to consider the effects of the compatibiliser on the interface. Figure 7-3 seems to indicate that despite compatibilisation, cohesive failure was occurring between the skin and core of the compatibilised materials. Clean nylon debris from the tensile testing appears to be clearly visible in the photograph, however as already noted

SEM analysis is subjective in interpretation and it cannot be stated without equivocation that the debris identified is nylon.

As injection speeds were increased a mixed layer began to form at the interface. This can be seen in Figure 7-4. This effect was previously reported by Akay [Akay, 1983] and Selden [Selden, 1998] in miscible systems of PP/ talc filled PP and immiscible PA/PP respectively. Again, this suggests that such a mechanism could also operate in the PP/PP system of earlier experiments.

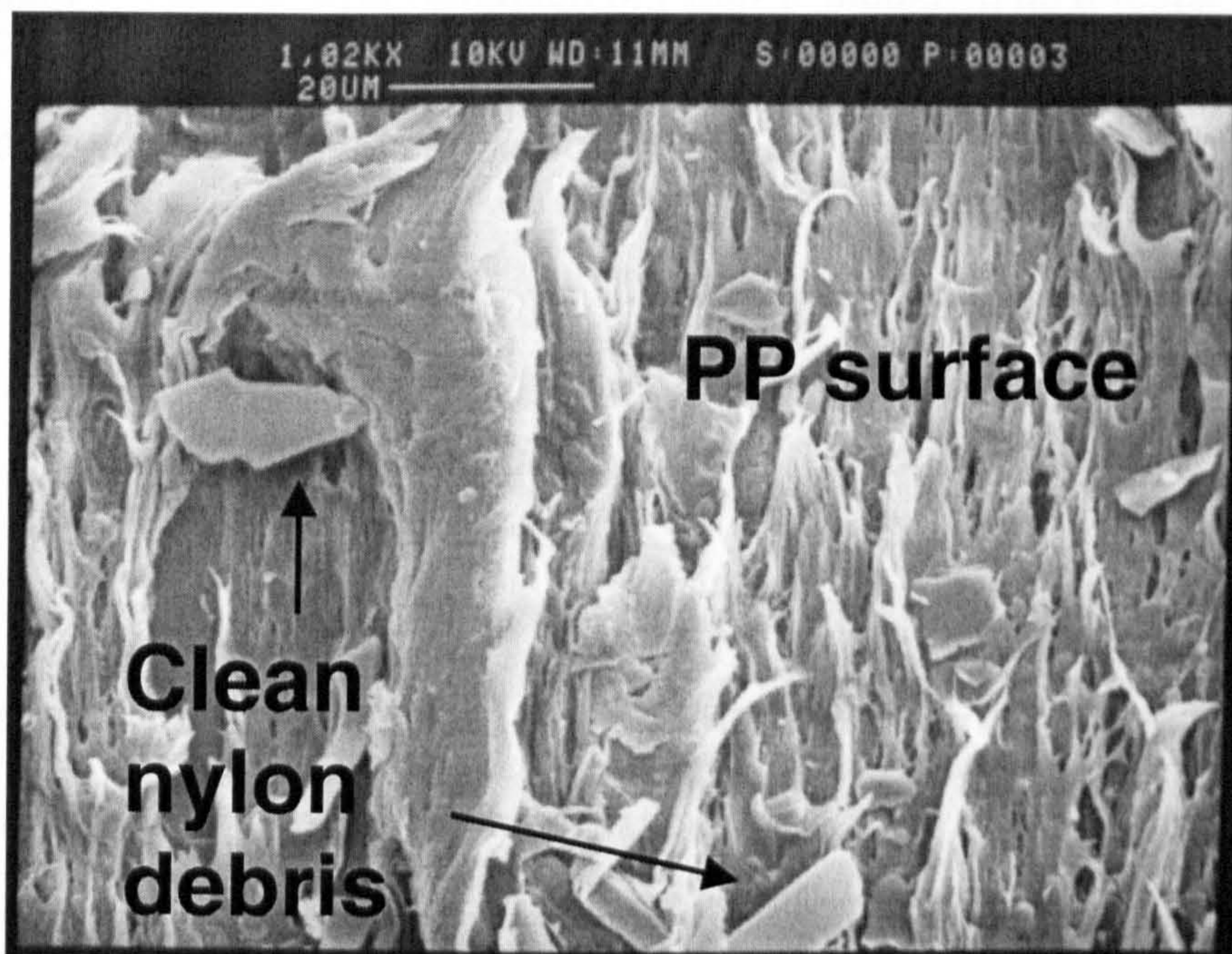


Figure 7-3 Fracture surface of PA6 skin, compatibilised PP core.

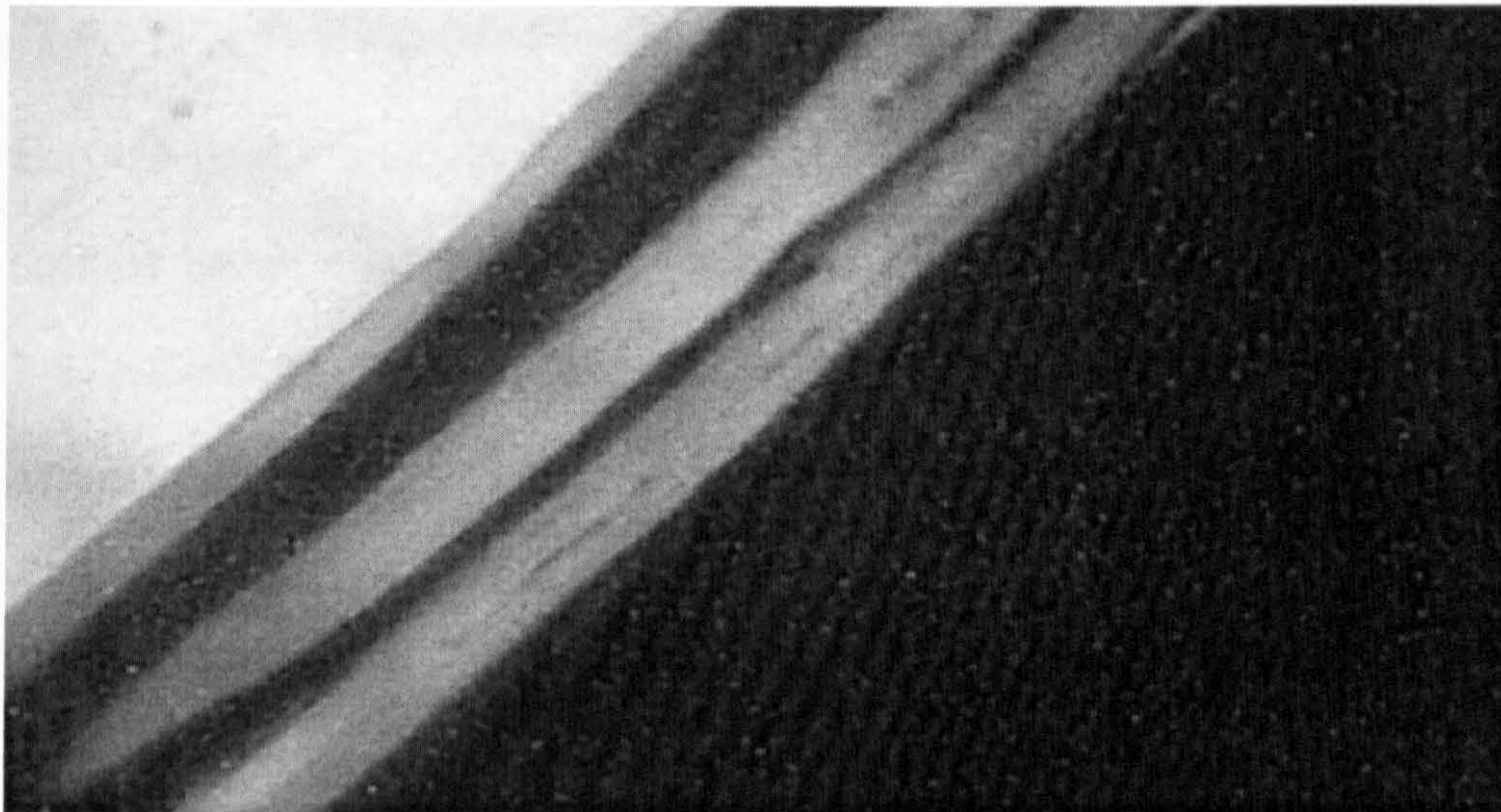


Figure 7-4 Mixed layer formation of PA6/PP moulding as a result of increased injection speed

[picture used by kind permission of J.C. Love, University of Warwick]

7.4 Processing effects on interfacial surface defects (Experiment 6)

To recap so far, experiments conducted to this point have been to examine possible causes of ridge formation and interaction at the skin/core interface during co-injection moulding. It appears there is a mechanism of polymer orientation at the skin/core interface not previously noted. There also appears to be a system of mechanical interlocking and ridge formation, but how these are related, if at all, it not yet clear. The next set of experiments therefore aimed to link the ridge to specific moulding parameters by attempting to quantify how they affected its size. The method chosen for this analysis was surface profiling.

7.4.1 Testing Justification

Surface profile analysis was chosen as it allowed a trace of the moulding surface which could be easily assessed visually such as shown in Figure 7-6, as well as providing quantitative data (Figure 7-5). Other methods of assessment were considered such as Surface Force Microscopy (SFM) and Reflective Interferometry (WYKO) However it was found that these methods sampled too small an area to be effective in this analysis because it is essentially longer wavelength features that need to be assessed.

7.4.2 Equipment

Surface assessments were carried out using contacting profilometry. The machine type was a Rank Taylor Hobson, Form Talysurf TM. This allowed a quantitative analysis of changes in topography of the surface of the injection moulding. The instrument has a 5µm diamond stylus tip and a meter cut of length of 8.00mm was used. A minimum of five profiles per sample were collected from positions along the line of polymer flow. Standard roughness parameters were determined from the software operating the profiler. Values presented in results tables such as 7-9 are averages of this data.

The parameter found to be most representative of the ridge was the peak to valley height, (Rt). As it was disturbances caused by the ridge on the surface finish that the project aimed to investigate and eliminate, this gave the most appropriate representation of the disturbance. A whole range of other data output was available, including parameters such as surface

roughness (R_a) , surface skew, (R_{sk}) and kurtosis (R_{ku}) the type of output being shown in Figure 7-5.

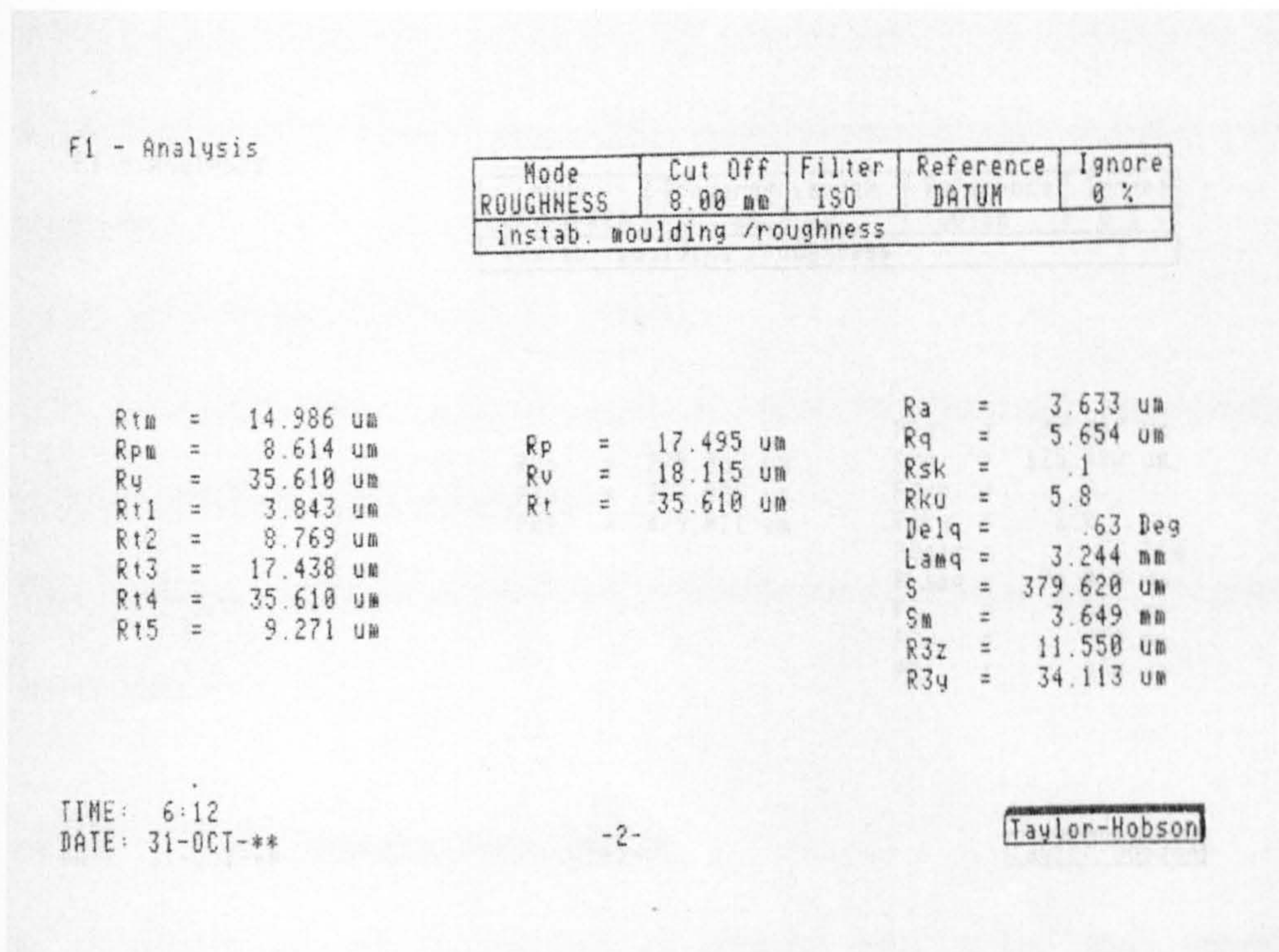


Figure 7-5 Example of data output from surface profile

As well as R_t , values of R_a are also given in the results tables, these being an indicator of the average roughness of the surface. This is the most commonly used representation of surface finish and since the ridge is an aesthetic defect R_a provides a useful indicator as to the quality of the surface finish. Many books are devoted to the study of surfaces. Further details on the derivation of these parameters and other parameters can be found in the reference works provided [Dagnall, 1986], [Whitehouse, 1994].

7.4.3 Tooling

The tooling used in this case is as shown in Figure 5-1, a centre fed sprue gated square plaque of dimensions 200 x 200 x 3mm.

7.4.4 Material

A transparent skin material (Nylon 12) was chosen. This allowed the core to be easily seen. The PP core was compatibilised to stick it to the nylon material.

Skin: EMS GRILON Nylon 12 TR90

Core DSM copolymer polypropylene stamylan P56M10 with 15% Uniroyal Polybond 3150 (compatibiliser)

The materials were predried prior to testing for 4 hours at 80°C to remove moisture.

7.4.5 Processing Parameters

A standard set of processing conditions was found that produced consistent mouldings. These settings are shown in Table 7-7.

Parameter	Setting
Melt Temperature Barrel A (°C)	250
Melt Temperature Barrel B (°C)	250
Mould Temperature (°C)	60
Injection Speed Barrel A & B (mms ⁻¹)	100
Holding pressure (on B) (bar)	50
set point (mm)	20
Holding time (sec)	15
Cooling time (sec)	40
Metering stroke Barrel A (mm)	63.5
Metering stroke Barrel B (mm)	60.0
injection delay on B (sec)	0.1
back pressure A & B (bar)	5

Table 7-7 Standard process parameters for Experiment 6.

The value of these parameters was then adjusted one value at a time whilst the other values were kept constant. The variable conditions for each parameter are shown in Table 7-8.

Parameter	Standard Setting	variable 1	variable 2	variable 3	variable 4
Skin/Core material Ratio	50:50	25:75	75:25	50:50	50:50
Mould temperature (°C)	60	20	40	80	60
Barrell Temp A(°C)	250	240	260	270	280
Barrell Temp B (°C)	250	200	220	260	280
Injection Speed A (mms ⁻¹)	100	25	175	250	290
Injection Speed B (mms ⁻¹)	100	25	175	250	290

Table 7-8 Variable parameters for Experiment 6.

7.4.6 Experimental Procedure

Plaques were produced in a random order for each of the settings shown in Table 7-8 to enable surface assessment measurements to be performed. After each parameter change, the first five mouldings were discarded.

7.4.7 Surface Profiles

Surface assessments were carried out as detailed in 7.4.2.

7.4.8 Result Summary :Moulding Surface Assessments

Test No.	Variable	Setting	Peak to Valley Rt (μm)	Roughness Average Ra (μm)
1	Skin:Core ratio	50:50	25.6	4.8
2		25:75	Unable to mould	
3		75:25	35.6	12.5
4	Mould Temp	20	25.4	4.7
5		40	25.6	4.8
6		60	24.6	4.8
7		80	22.9	4.8
8	Barrel Temp A	240	25.8	4.7
9		250	24.5	4.6
10		260	25.7	4.7
11		270	24.3	4.7
12		280	23.6	4.5
13	Barrel Temp B	200	22.7	4.7
14		220	24.8	4.7
15		250	23.5	4.7
16		260	25.2	4.6
17		280	23.9	4.7
18	Injection Speed A (B speed 100)	25	26.8	5.3
19		100	25.8	4.6
20		175	25.4	4.7
21		250	24.5	4.5
22		290	25.7	4.7
23	Injection Speed B (A speed 100)	25	25.1	4.7
24		100	25.3	4.7
25		175	28.2	8.3
26		250	32.1	9.0
27		290	5.5	2.7

Table 7-9 Results for Experiment 6

The compatibilised interface produced surface defects. Surface profile measurements allowed quantitative data about its shape and enabled the effect of moulding parameters on it to be deduced. A typical example of the shape of the profile produced is shown in Figure 7-6.

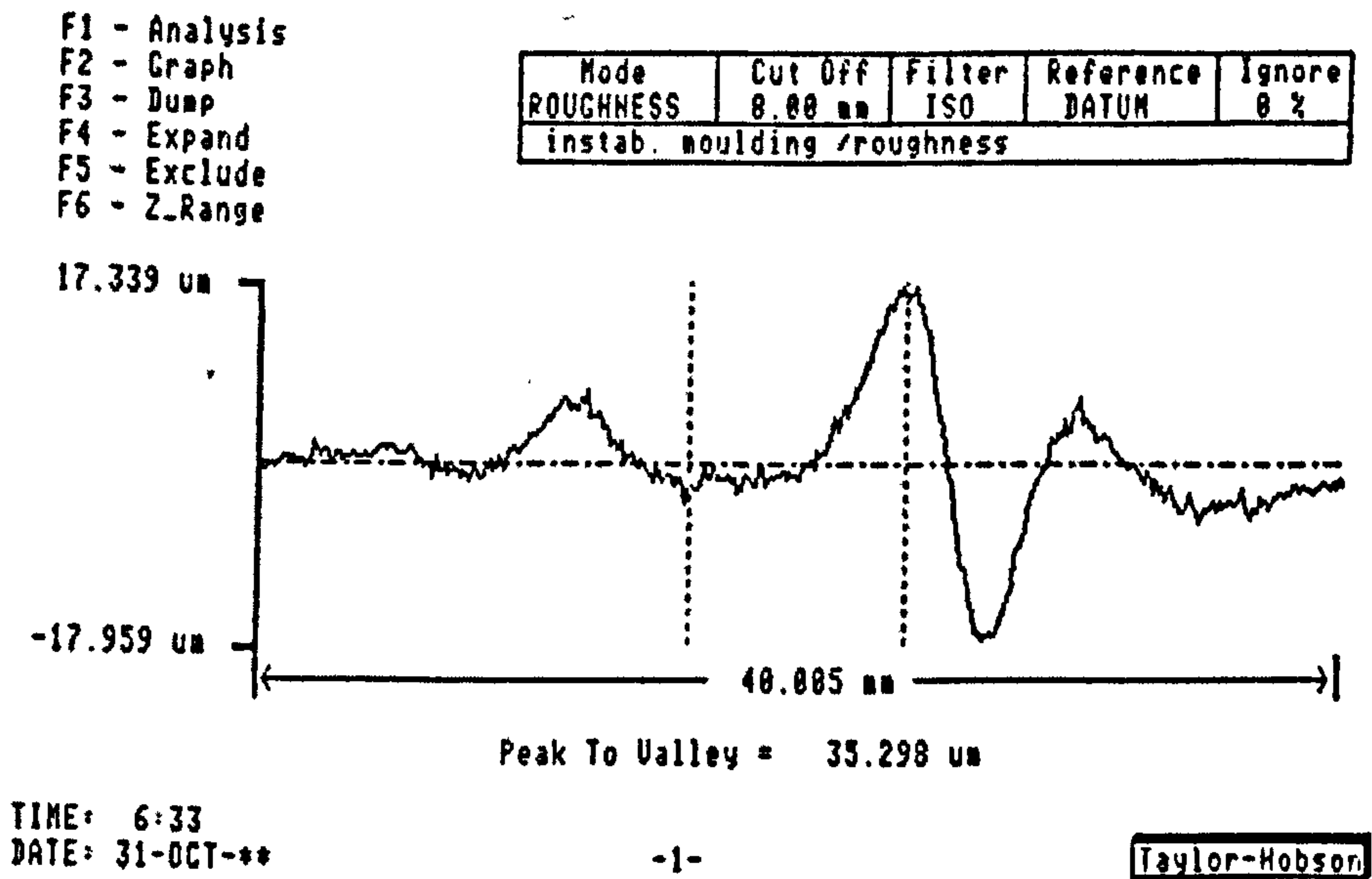


Figure 7-6 Surface profile from interface of skin and core

7.5 Surface Profile Analysis

The overall shape of the profiles taken at the skin/core interface were ridge like in appearance and this appears to be standard for all systems investigated. The direction of material flow relative to Fig 7-6 is right-left. Producing a characteristic bump and dip. This suggests there may be a mechanism of material displacement taking place.

The results of the parameters assessed (melt temperature, mould temperature and relative injection speeds) are shown in Table 7-9. Only injection speeds seemed to have an effect. The relative amounts of skin and core in these cases were kept at 50:50. It appears that as the mixed layer such as the one shown in Figure 7-4 begins to form, the ridge gives way to form a flatter and less undulating surface finish.

The change also appears to be related to a specific range of injection speeds between 200 and 250mms⁻¹.

With the 'halo' type effects seen in PA12/PP systems, a difference in the orientation of the material in the region of the interface is visible and is caused by the inability of the melt stream to recover from the stress changes caused at the meeting of the flow fronts. Dharia notes a similar effect in injection moulding of material blends [Dharia, 2000]. Why the ridge would form only at the flow front and not along the whole interface will now be examined.

7.6 The Interface

It is believed that the reason a ridge only occurs at the flow front interface is due to the differences between flow along the plane of the skin/ core boundary and that at the point at which the flow fronts meet. Stresses can occur in a number of directions as shown in Figure 3-9. Two positions of flow fronts are identified in Figure 7-7. In the second position we find in effect stratified flow. There is little interaction of the flow fields in the

direction of flow (y plane) and therefore also little interaction in the first normal stress. Gradients exist in terms of shear, pressure and temperature at this position on the interface (see Figure 6-10), but no interaction occurs between skin and core except for molecular diffusion. Stresses at this point will include some elongational stress and a shear component dependent upon the relative speeds of the skin and core flow. The amount of slip between skin and core will also affect the relative level of shear. This is in effect what is seen in co-extrusion.

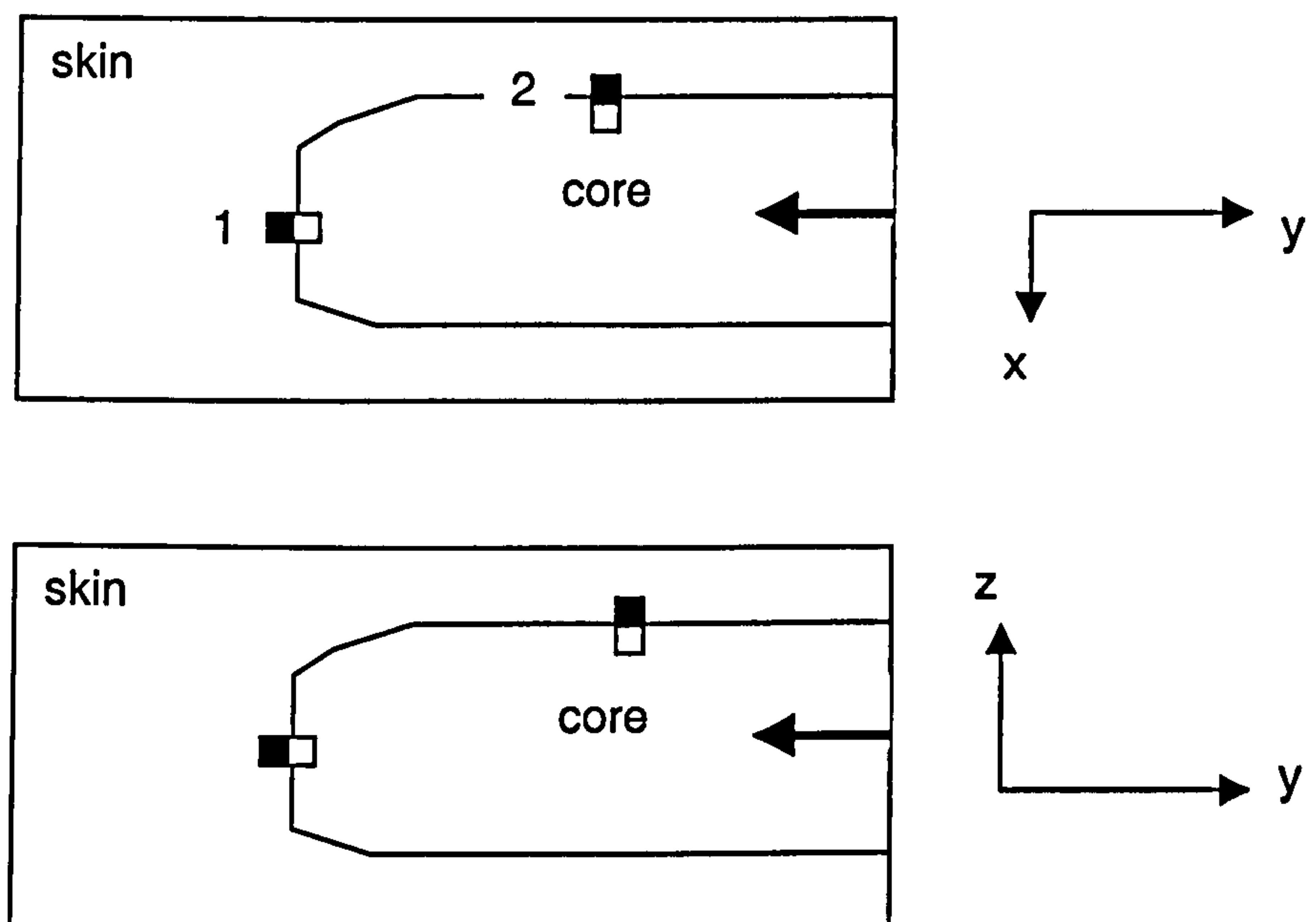


Figure 7-7 Differences in normal stress interaction of skin and core at two positions during co-injection moulding.

However, unlike in co-extrusion systems, there is the point where the core molten flow stops pushing the skin ahead of it. This is shown in Figure 7-7 as position 1. As the mould fills, skin and core contact, flowing in both the same direction and same plane. The pressure on the core exerts a force on the skin material and pushes it forward. At the point the mould

completely fills, a force from the skin back onto the core stops forward flow. At this point first normal stress differences at this interface become of major importance. What occurs at this point will control the interaction between the core component and that of the skin component. A major factor influencing this interaction will be the relative speed at which the melt fronts 'collide'. For movement to stop equal and opposite forces must apply as shown in Figure7-8. Therefore, despite the fact there may be very high compressive stress at the interface there can be little or no movement of the flow. This will be the result of the interaction between injection speeds, material viscosity and the pressure in the cavity. For example if the core is of lower viscosity than the skin and the core moves towards the melt front, the effective melt flow velocity will increase due to an increasing pressure gradient resulting from a reduced effective flow length.

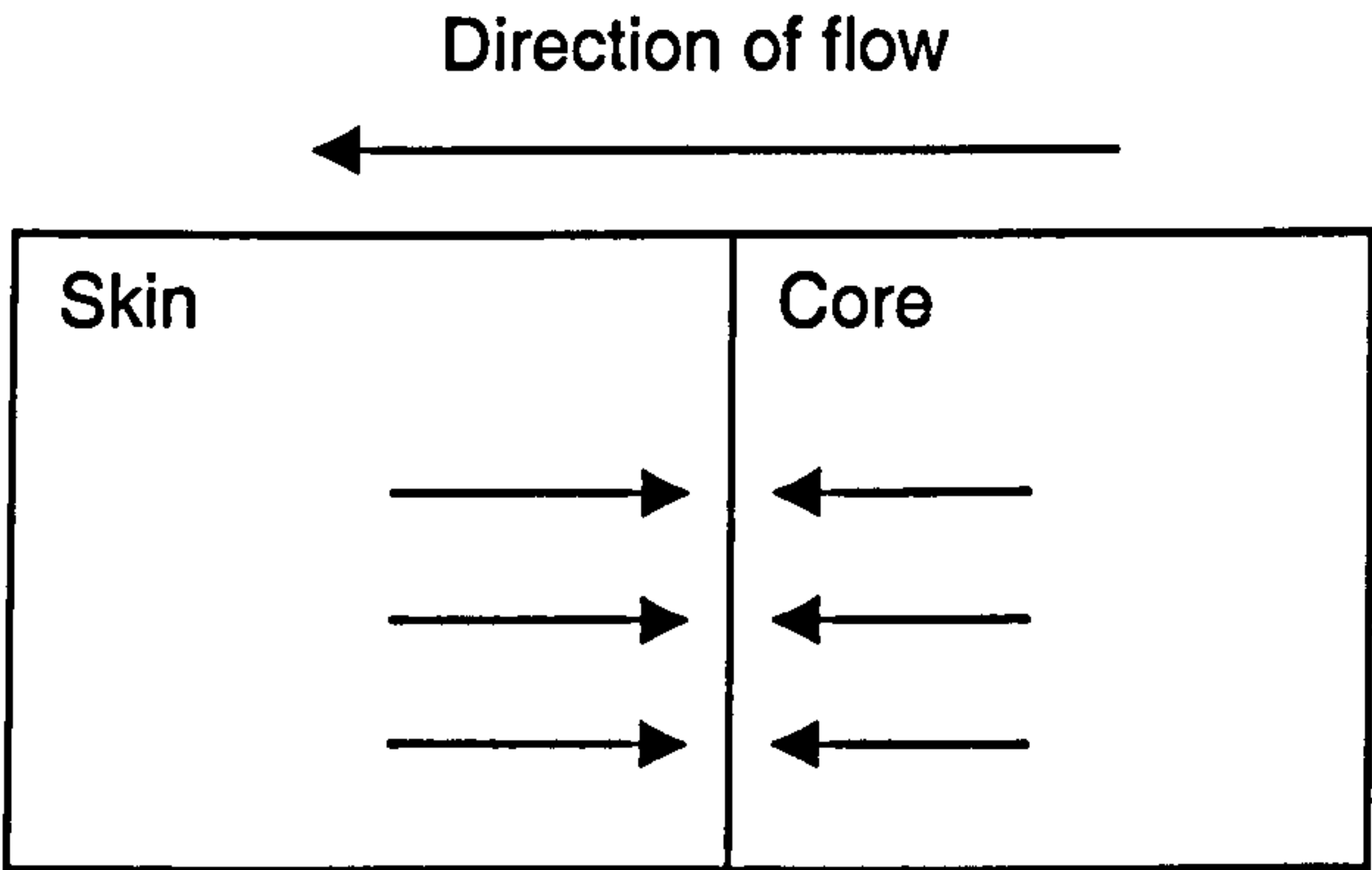


Figure 7-8 Forces must be equal at skin /core interface to prevent flow

7.6.1 Normal and Shear Stresses at the interface

Viscoelastic stress differences at an interface such as shown in Figure 7-8 will create a disruption and non-equilibrium conditions will exist at this point. As previously discussed, this is primarily the result of first normal stress differences but the flow also has a component of elongation, which affects the second normal stress. The larger the magnitude of the difference in the stresses, the greater the effect will be. In addition, there will also be shear effects, as the two layers interact. The point of highest shear rate concentration will vary with the material properties and their processing history. This means that the point of highest shear may be concentrated in either the skin or core components as reported previously [Kadota ,1999].

7.6.2 'Internal Weld-lines'

On further examination the ridge appeared very similar to defects caused by weld-lines in mouldings caused when two flow fronts collide within an injection moulding tool such as shown in Figure 7-9. In this case however the flow fronts are meeting below the surface of the moulding to produce an 'internal weld-line' as shown in Figure 7-10. Weld-lines are the result of the spitting and recombining of melt flows. How the materials recombine is dependent on diffusion, chain entanglement and mixing. These are the same type of effects discussed in experiments on the co-injection moulded PP/PP systems of Chapter Five.

These types of mechanisms are in turn affected by factors such as the temperature of the molten flow, flow speed and direction of the flows [Chang, 1999]. The level of 're-combination' will affect the strength of the weld-line. Interestingly, weld-lines are often found to have a 'v' notch formation at the surface and a ridge on either side of the flow [Chang, 1999]. This ridge is formed by the inability of the melt stream to fully re-combine. In the case of the ridge in this co-injection study, the meeting flow fronts are unable to dissipate built up stresses across the interface just as two separated polymer melts cannot re-entangle and seamlessly re-mould and instead form a weld-line. The mechanism is similar but there are also differences.

A weld-line is the result of separated molten flow being re-combined. The ridge is the result in two flow fronts with different properties (such as speeds) coming together. In a similar fashion to the halo effect described earlier, the ridge is the result of melt instability. However, the analogy of the weld-line is useful to further develop the idea of the part played by diffusion and chain-entanglement in miscible co-injection moulding systems.

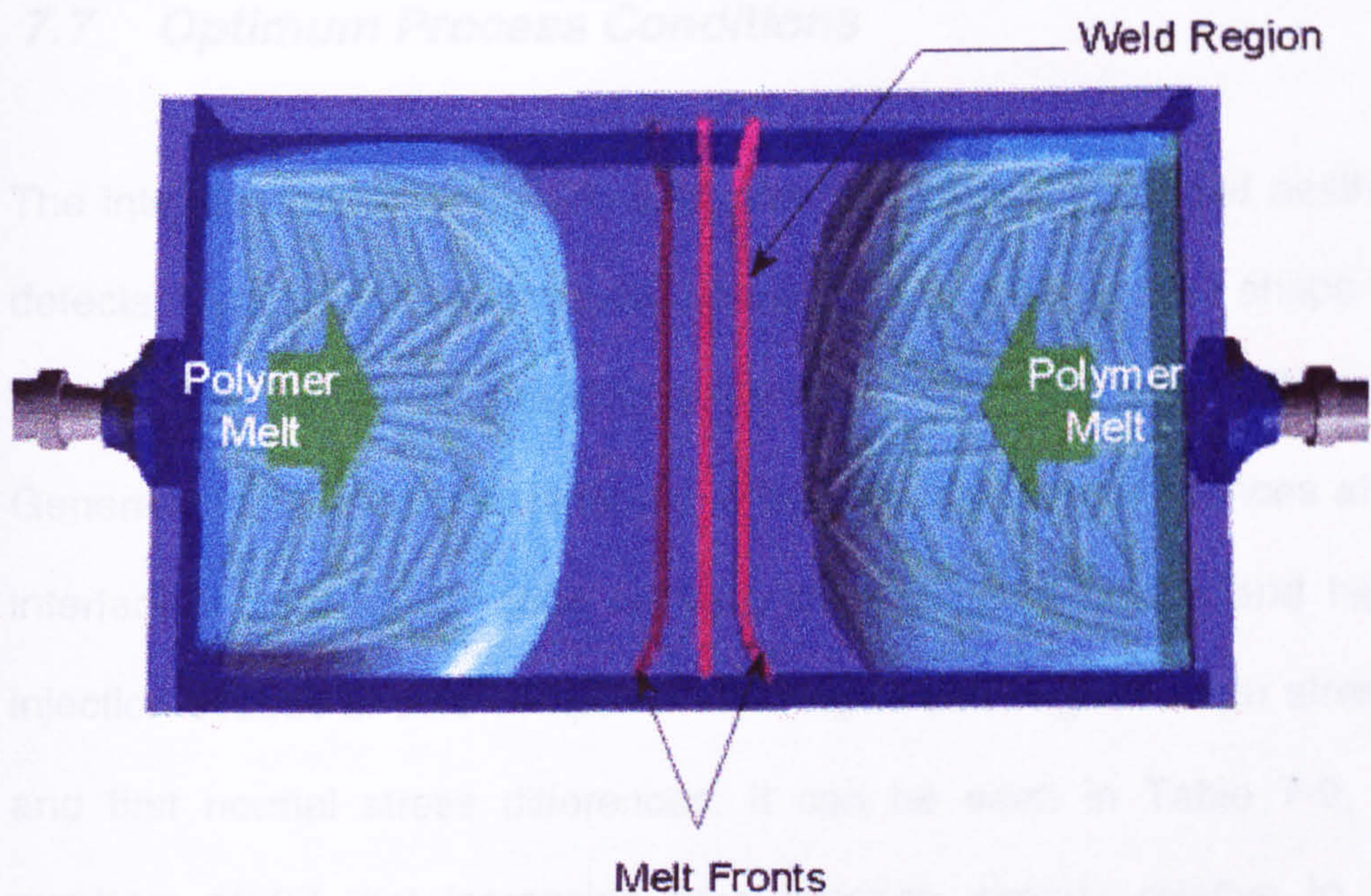


Figure 7-9 Weld-line formation

[Source: http://islnotes.cps.msu.edu/trp/inj/geo_weld.html, accessed 9/8/01]

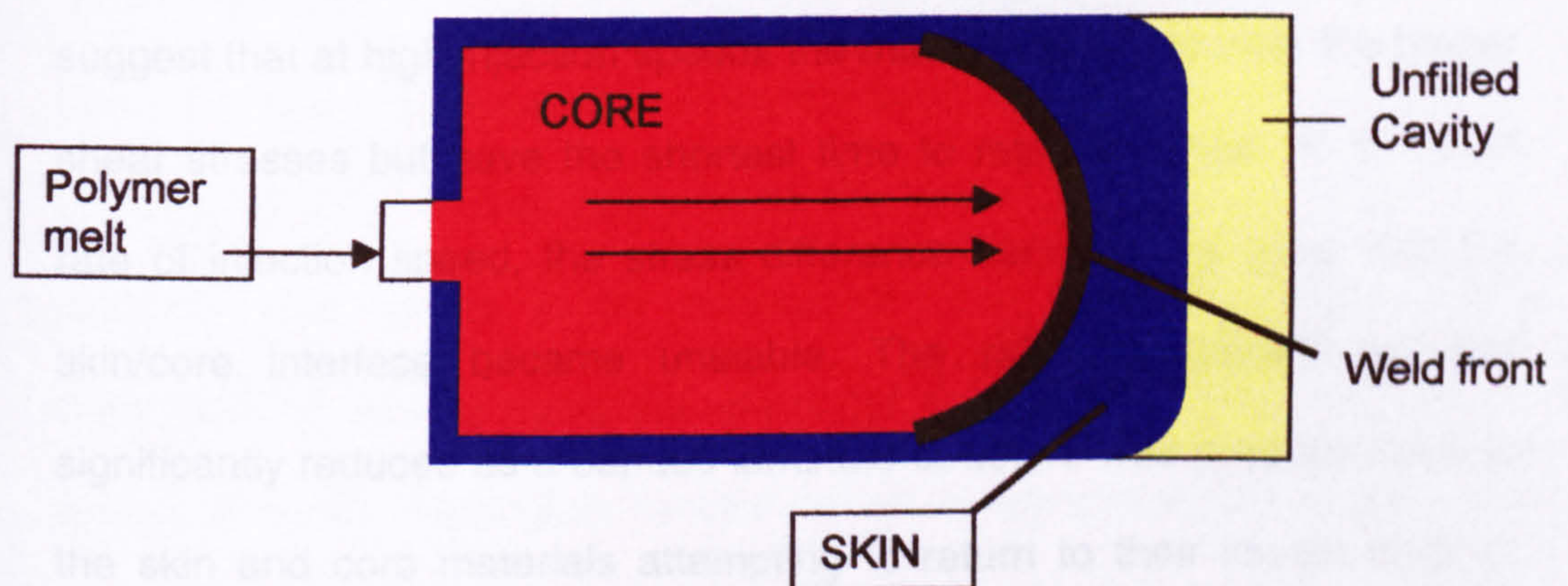


Figure 7-10 Formation of internal weld-line

7.7 Optimum Process Conditions

The interface between the skin and core components produced aesthetic defects. Surface profilometry gave quantitative data about their shape and enabled the affect of moulding parameters on them to be deduced. Generally factors which contributed to building in stress differences at the interface increased the ridge i.e. long core injection delays and higher injection speeds of core component leading to both higher shear stresses and first normal stress differences. It can be seen in Table 7-9, test numbers 18-27 that increasing core injection speeds relative to skin injection speed had the greatest effect but only within certain limits. As speed increased, a point was reached where the ridge seemed to disappear. Values of R_t and R_a at this point are very low. These results suggest that at high injection speeds the material will encounter the higher shear stresses but have the shortest time to relax stresses. At a critical rate of injection speed, the stress difference becomes so great that the skin/core interface became unstable. The ridge disappears or was significantly reduced as a banded laminate structure was produced due to the skin and core materials attempting to return to their lowest level of internal stress.

This evidence suggests that it is not viscosity differences causing the ridge since no change in temperature and hence change in viscosity is taking place during this change. However, it could be argued that by increasing

speeds, shear heating is increased that will have the affect of lowering the viscosity of the material. However, for this increase to be large enough to cause a ridge in a single polymer system would require the occurrence of a large temperature difference. If viscosity were a major factor, experiments varying melt temperature would also be expected to yield the effects. It is therefore more likely that it is the relief of stress differences in the skin and core component causing the problem.

In theory, factors that allow recovery of stresses or prevent stress differences in the first place i.e. slow core injection speeds and similar skin/core viscosities prevent or reduce ridge formation. This effect was not seen in these particular sets of experiments on PA12 and PP. It is possible the moulding parameters required for these moulding conditions fall below those encountered in current moulding technology. It may however have been possible to repeat these experiments using materials of similar viscosity. This is difficult however as the effect of the compatibiliser on viscosity also needs to be considered. This requires compounding equipment to ensure adequate mixing of the PP and compatibiliser to enable accurate rheological measurements to be undertaken [Goodship, 2001 b] but this was not available to this project. However work previously reported by Goodship and Kerwin [Goodship, 2001 a] on a miscible system of an acrylic skin and a polycarbonate core of similar viscosities found instabilities could be induced with increased injection speeds. This further supports the postulated hypothesis.

Also, if it is considered that mouldings made of material of similar viscosities and speeds do not produce a ridge under 'normal' moulding conditions in miscible systems it can be argued that these show that stress dissipation or lack of stress differences prevent ridge formation.

Conclusions reached from this set of experiments on compatibilised PA12 /PP systems indicate that interfacial bond strength produced by compatibilisation is lower than interfacial bond strength of the weld-line. So while previous research in peel testing can give an estimation of interfacial adhesion [Rungseesantivanon 2000], [Selden, 1998] it has not previously revealed the weakness of the bond in compatibilised mouldings. This is a novel finding.

The series of experiments using polypropylene as both skin and core (see Chapter 5), suggest strongly that diffusion and chain entanglement is the primary mechanism of bonding between skin and core. When this is limited, even when a chemical bond in the form of a compatibiliser is used, the interface shows considerable weakening, as borne out in the weld-line experiments. The strength of the bond produced by the reduced diffusion and entanglement at the weld-line still exceeded the strength of the chemical bond produced by the compatibiliser.

Processing parameters have little effect on the height of the ridge, except for increased injection speeds. At a certain speed a mixed layer forms at the interface, which has bonding properties exceeding those of the standard interface, the ridge also dissipates at this point. Increased injection speed is also linked to an increase in normal stress. The effects

of normal stresses on the interface have now been shown and explanation given as to why the ridge occurs only at the flow front. It is the author's belief that these are novel findings.

For systems with miscible components, it appears that the effect of viscosity ratio is greater than the effect of normal stress in terms of controlling the degree of interaction at the interface. Stresses are able to dissipate by relaxation across the interface under typical moulding conditions. If very high levels of normal stress differences are induced at the interface however, ridge type effects and therefore stress differences become of importance. Once diffusion is limited or removed, normal stresses and injection speeds control the reaction between the skin and core melts as the core to some degree 'bounces' off the skin when the melt fronts meet. These effects are less dependent on parameters such as temperature because normal stress relationships are independent of temperature whereas relationships such as skin/core viscosity are not.

Chapter 8. Developing a process route to eliminate surface distortions whilst promoting bonding between skin and core

8.1 *Introduction*

The final part of the experiments looked at developing a method where the interface did not rely on chemical adhesion alone and mechanical interlock was introduced at the interface. Whilst this can be achieved simply by incorporating glass fibres into the core component, it had been noted in injection moulding trials that increased mixing could be induced by increased injection speeds. This produces the mixed layer noted in the research of Akay [Akay, 1983] and Selden [Selden, 1998] and also found during the course of this research. It was also found formation of these mixed layers seemed to prevent formation of the surface ridge defect associated with the PA12/PP system. Therefore, this offered the possibility of improving the properties of not only compatibilised systems but also to promote the bonding between immiscible skin and core components without the use of a compatibiliser.

This work has since shown that compatibilised mouldings have a weaker interface at the boundary between skin and core than that produced at the weld-line of two identical melts. The use of compatibilisers for co-injection moulding must therefore be called into question. Selden [Selden, 1998] also found that his un-compatibilised samples with a mixed layer had

flexural properties as good as those that were compatibilised. Since compatibilised mouldings showed both aesthetic defects and a drop in tensile properties at the interface, the addition of compatibiliser appears not to have much effect except as a weak tie layer providing the bulk properties of surface layer only. Whilst this could still find use in applications such as in-mould coating where only limited adhesion may be acceptable, alternative methods which eliminated costly compatibiliser now seem to be an attractive possibility.

Mechanical interlocking is one such alternative way of obtaining adhesion between polymers. Therefore the final set of experiments looked to mechanically interlock an immiscible system of polystyrene and high density polyethylene by attempting to control the mixed layer development system. These materials were chosen for two reasons. Firstly, since this work is novel, a combination used by researchers in co-extrusion studies was chosen in the hope of providing comparison with this data. Secondly, the use of a brittle polystyrene skin meant it was possible to crack open the moulding and pull the polystyrene component away from the HDPE. This allowed comparisons to be made whilst moulding trials were in progress.

8.2 Experiment 7: Study on Non-miscible Systems

8.2.1 Tooling

For these experiments a centre gated, sprue-fed square plaque of 200mm x 200mm x 3mm as shown in Figure 5-1. This allowed a large symmetrical area for material flow and measurement.

8.2.2 Material

The material used was an injection moulding grade of polystyrene, BP Polystyrene HF555, MFI 22. The core was a commodity HDPE, DSM Stamylan High density polyethylene 7625 , MFI <1. This was dosed with a low dosage (1%) of a commercially available blue masterbatch. This allowed skin and core to be distinguished as well as enabling any material bonding on the polystyrene to be clearly seen.

8.2.3 Processing Parameters

The moulding parameters used are shown in Table 8-1.

Parameter	Setting
Melt Temperature Barrel A (°C)	220
Melt Temperature Barrel B (°C)	220
Mould Temperature (°C)	40
Injection Speed Barrel A & B (mms ⁻¹)	100
Holding pressure (on B) (bar)	50
Set point (mm)	20
Holding time (sec)	15
Cooling time (sec)	40
Metering stroke Barrel A (mm)	63.5
Metering stroke Barrel B (mm)	60.0
Injection delay on B (sec)	0.1
Back pressure A & B (bar)	5

Table 8-1 Standard Process Parameters for Experiment 7

The values of these parameters were then adjusted one at a time while the other values were kept constant. The variable conditions for each parameter are shown in Table 8-2.

Parameter	Standard Setting	variable 1	variable 2	variable 3	variable 4
Skin/Core material Ratio	50:50	25:75	75:25	-	-
Mould temperature (°C)	40	20	60	80	-
Barrell Temp A(°C)	220	200	240	260	-
Barrell Temp B (°C)	220	200	240	260	-
Injection Speed A & B (mms ⁻¹)	100	25	175	250	290

Table 8-2 Variables for Experiment 7

8.2.4 Experimental Procedure

The mouldings were produced in a random order to eliminate any order effects and then mouldings were split apart to look for any sign of interfacial mixing. Equipment and test methods were as used previously and are described in sections 7.4.1 and 7.4.6. Interlocking was considered present if blue bands of material could be clearly seen in the transparent skin material such as shown in Figure 8-4. The presence of interlocking made it difficult to assess the polystyrene surface, therefore in Table 8-3 there are no profile results for these mouldings. At 175mms⁻¹, interlocking was irregular and patches of the surface could be assessed.

8.2.5 Results

Polystyrene Interface assessment

Test No.	Variable	Setting	Polystyrene Peak to Valley Rt (µm)	Roughness Average Ra (µm)	Interlocking Y/N
1	Skin:Core ratio	50:50	40	12.1	N
2		25:75	31	12.4	N
3		75:25	-	-	Y
4	Mould Temp	20	33	13.4	N
		40	45	13.7	N
5		60	40	12.8	N
6		80	55	13.9	N
7	Barrel Temp A	200	55	13.1	N
8		220	58	13.9	N
9		240	60	13.7	N
10		260	74	14.1	N
11	Barrel Temp B	200	55	13.4	N
12		220	54	12.8	N
13		240	62	13.3	N
14		260	73	12.2	N
15	Injection Speed A & B	25	50	13.5	N
16		100	45	12.6	N
17		175	133	20.5	Y
18		250	-	-	Y
19		290	-	-	Y

Table 8-3 Results for Experiment 7

8.3 Discussion

The results of the surface analysis can be found in Table 8-3. It can be seen that only changes to skin/core ratio and injection speed produced significant effects.

8.3.1 The Effects of Injection Speed

As expected, at low injection speeds of 25mms^{-1} the lack of adhesion was readily visible and the polystyrene came away cleanly from the HDPE. Shrinkage differences at this stage caused very visible distortions of the mouldings. However as the injection speeds were increased to 175mms^{-1} , the mouldings showed less tendency to distort as some level of interfacial mixing began to happen at the onset of non-laminar flow. This has implications for both conventional and co-injection moulding as it suggests that the mechanisms of mould filling, that being fountain flow, do not impart interfacial mixing properties and hence adhesion, on skin and core components. Further, it implies that if plastication has failed to homogenize the molten material, the properties of the melt are unlikely to be dispersed through small scale interfacial mixing mechanisms during filling. The size of the peak to valley height rises significantly at this point and a sample from these mouldings is shown in Figure 8-1. A banded structure is clearly visible and the pattern appears oscillatory in nature. It is interesting to consider that a surface profile of this effect shown in Figure 8-3 bears a resemblance to the pressure fluctuations in rheology measurements during melt fracture. An example of such a trace is shown in Figure 8-2 and was produced on a capillary rheometer. It is also interesting to note that the shear range for melt fracture is at a similar level to those experienced at the gate of the injection moulding tool used for this trial. For example using the formula introduced in section 3.2.3., the

maximum shear at the injection gate is 2500 s^{-1} . When the same HDPE sample was subjected to this level of shear in a capillary rheometry, an oscillation in the pressure was clearly seen (Figure 8-2).

According to Aggasant [Aggasant,1991], the phenomena of melt fracture and interfacial instabilities are unrelated. However, the appearance of irregularities in the melt stream at a certain shear would suggest that stratification of properties is the root cause of both phenomena.

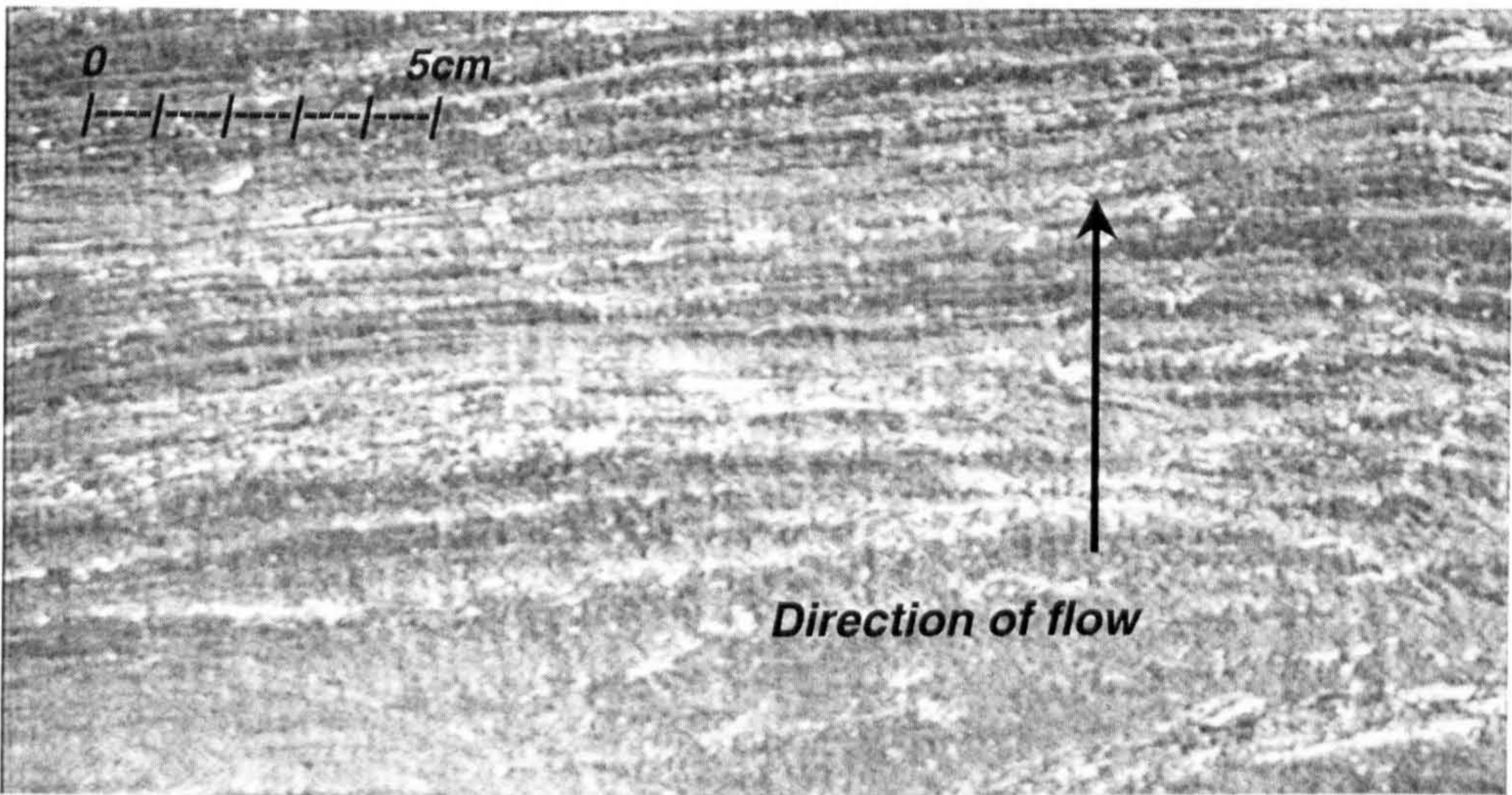


Figure 8-1 Banded Structure of Polystyrene interface

Figure 8-2 Surface variations measured at the PS gate

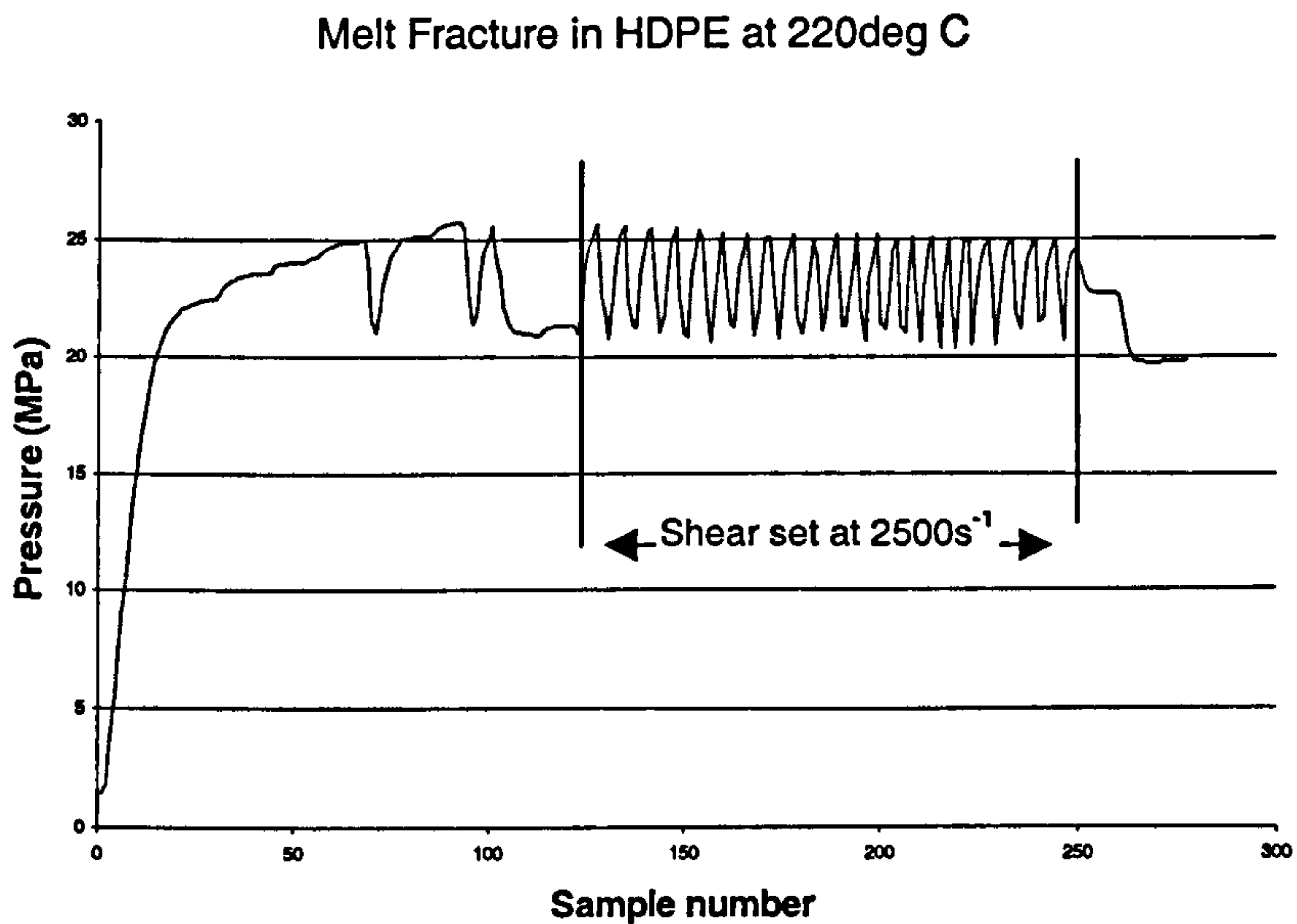


Figure 8-2 Pressure fluctuations during melt fracture of HDPE

[The sample number in this figure relates to specific shear settings. Each of these stages can be programmed individually to specific levels of shear rate, to ramp the shear rates up and down or hold specific levels as shown here]

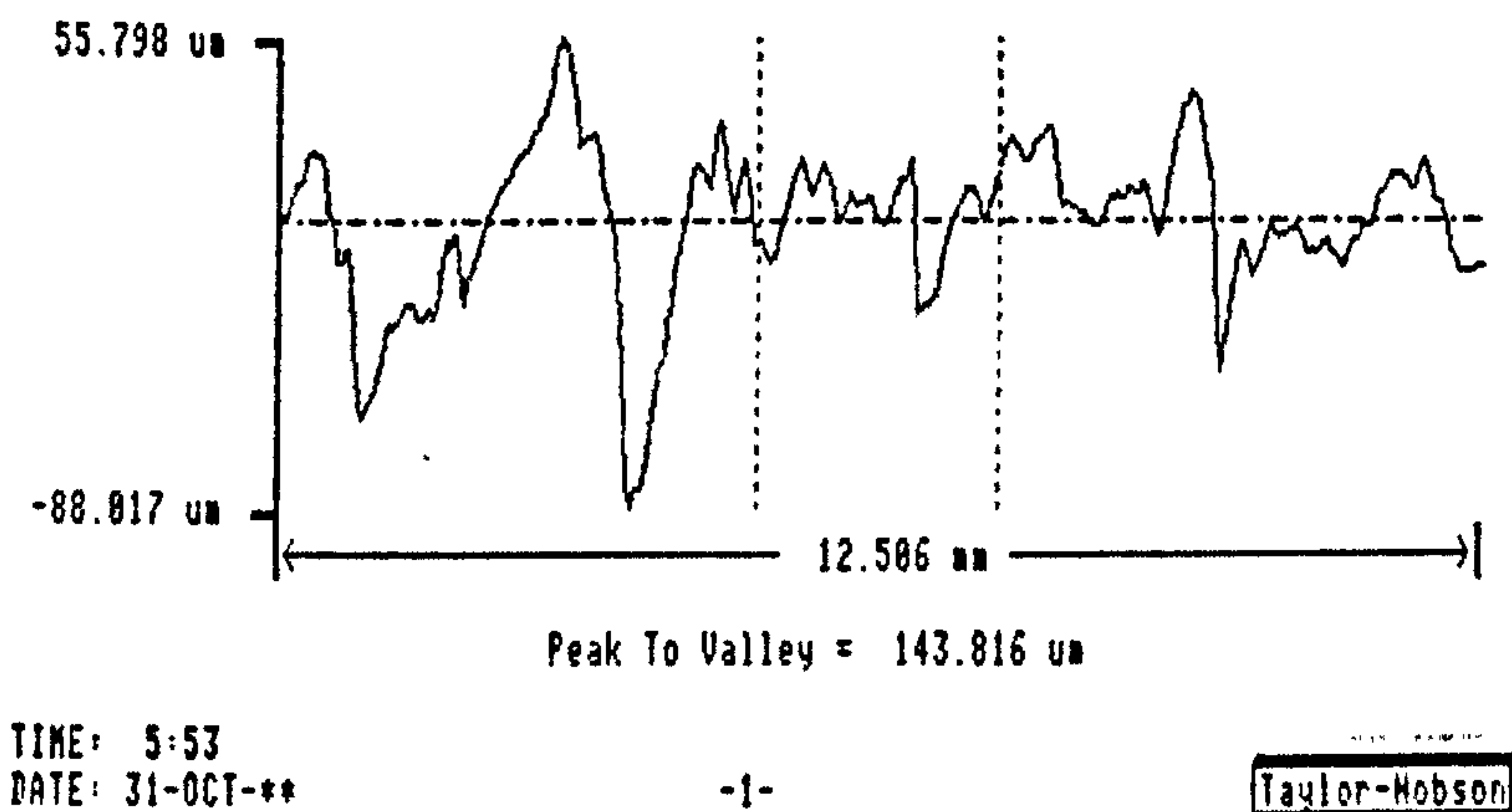


Figure 8-3 Surface Variations measured at the PS interface

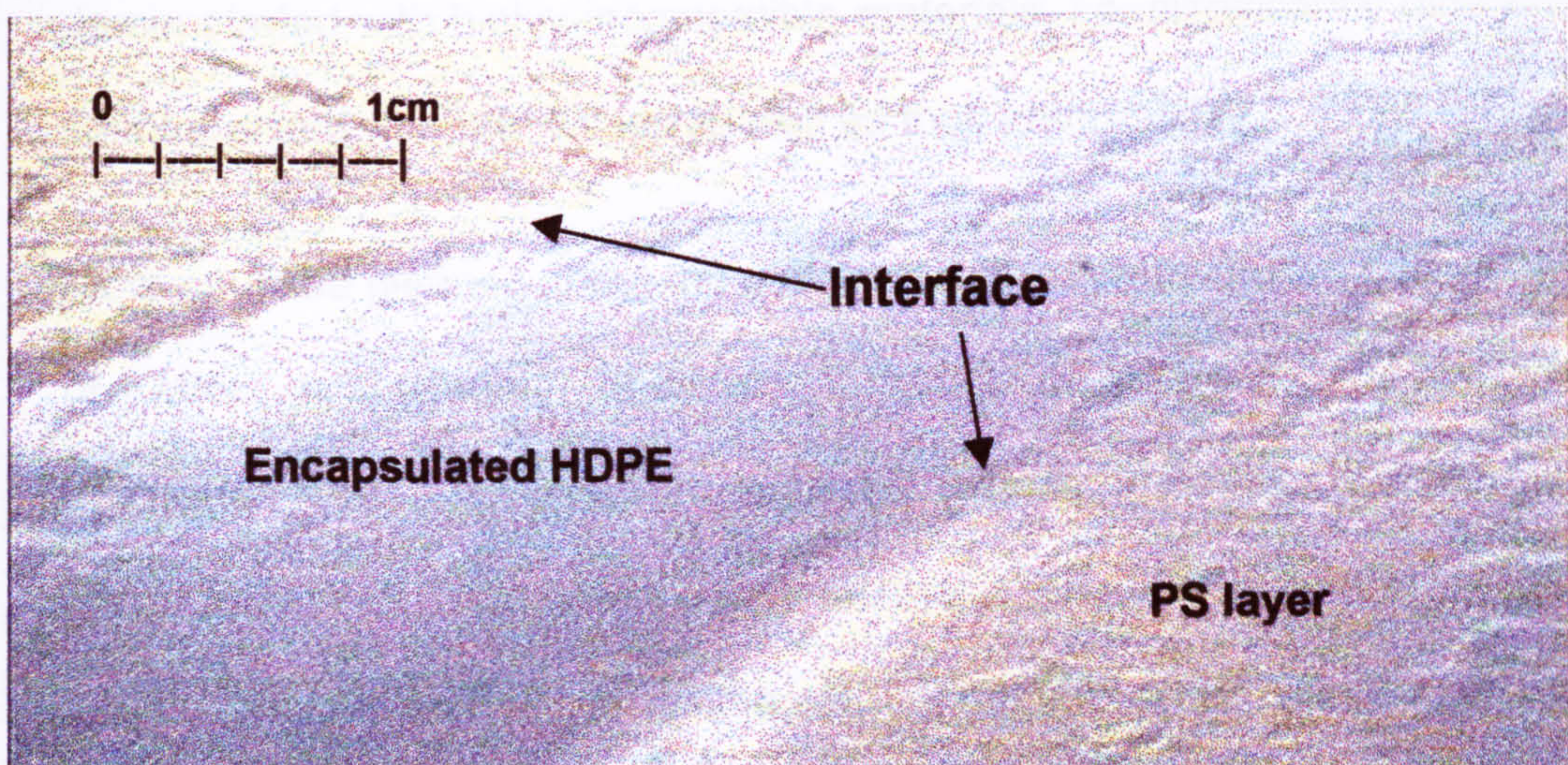


Figure 8-4 Encapsulation of HDPE by Polystyrene

At speeds of 175mms^{-1} it was possible to still peel away the polystyrene skin, however a thin layer of HDPE was clearly visible on the surface. This can be seen in Figure 8-4 with the HDPE showing as a darker region.

There were no ridges at the skin/core interface in this system as had been seen in the compatibilised materials. At higher speeds, a locking mechanism became more apparent and the core could be induced to penetrate near the gate region by a slight reduction of the injection speeds towards the end of mould filling. (Injection speed profiling was discussed in section 2.1.2.). This presumed that this reduced shear effects in this area. The formation of a mixed interfacial layer of polystyrene and HDPE shows promising initial results for using this method to produce multi-material mouldings with good inter-layer bonding without the use of compatibiliser and without a surface defect. This is impressive given that it was

demonstrated with highly incompatible materials, i.e. significantly different shrinkage and viscosity values as well as their immiscibility,

More could be gleaned about the effects of relaxation by studying the work of Kadota et al [Kadota, 1999] who looked at orientation of PP and PS components at a co-injection moulded interface. Optical microscopy, microbeam-WAXS and birefringence techniques were used by Kadota and it was reported that with a co-injected interface of a PP skin and a PS core, the PP orientated at the interface as a result of shearing flow from the PS. In the reverse scenario with PP as a core, the orientation levels at the PP interface were low, this being attributed to increased cooling and hence increased stress relaxation time. Using higher core speeds, shear heating results in more shearing and orientation in the PS skin interface. This suggests that orientation differences may be dependent upon which material is in the skin and which is in the core. This also provides further evidence for the hypothesis of different shear and cooling regimes occurring in both the PP/PP and mixed systems. However, from the work of Kadota et al, it is not clear what feature of the material creates this difference.

8.3.2 The formation of mechanical interlock

The formation of the mechanical interlock that was visible in Figure 8-4 is shown diagrammatically in Figure 8-5. The first stage is a change from laminar flow to an oscillatory flow as shown earlier in Figure 8-1. Bending of the wave peaks can then result both from shearing flows across the

wave front, which bend the flow fields and viscosity encapsulation phenomena, which was discussed in Chapter Three. This wave development is shown in Figure 8-6. This leads to encapsulation and mechanical interlocking such as shown in the PS/HDPE mouldings as in Figure 8-4.

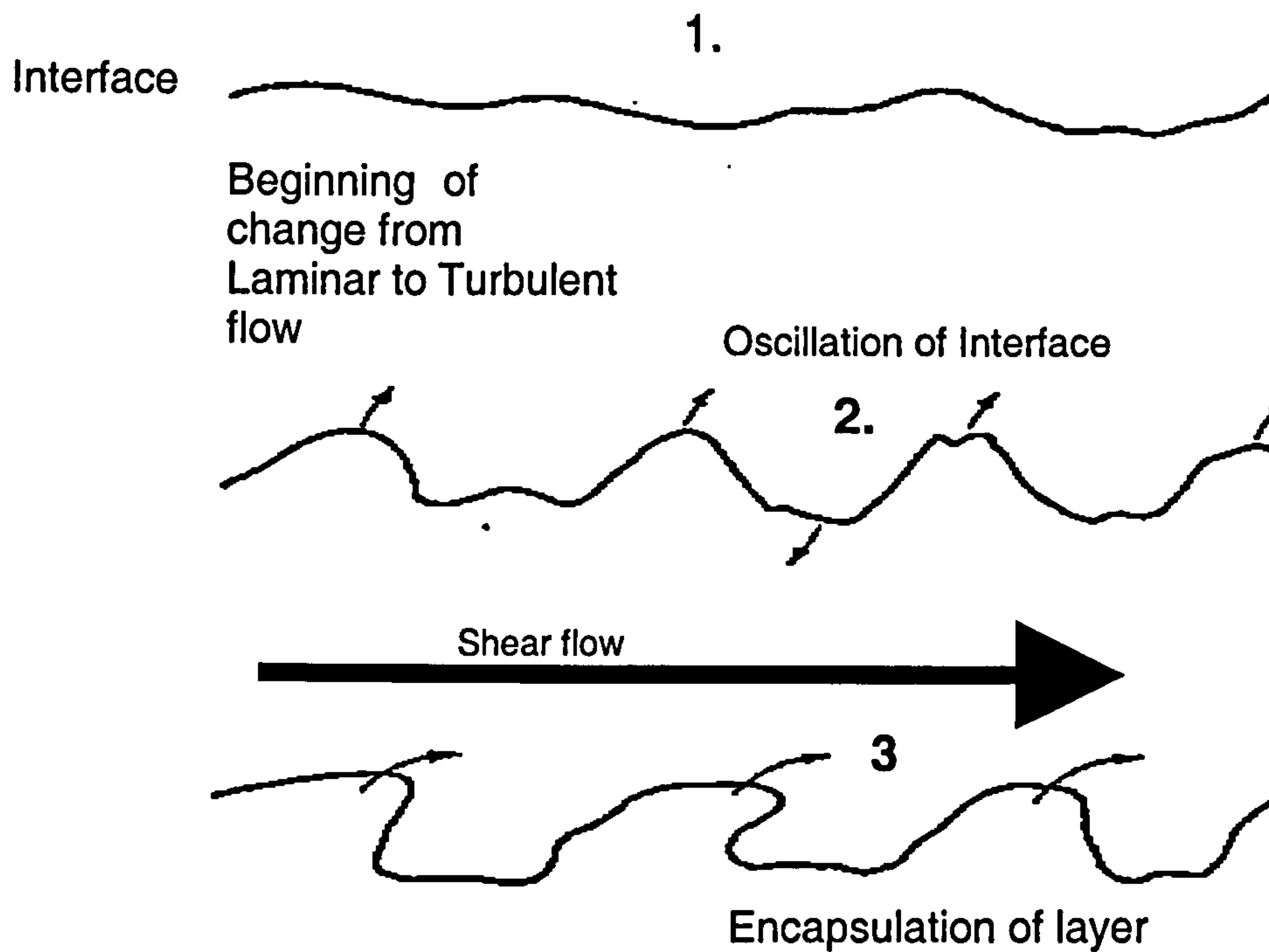


Figure 8-5 Mechanism of mechanical interlock

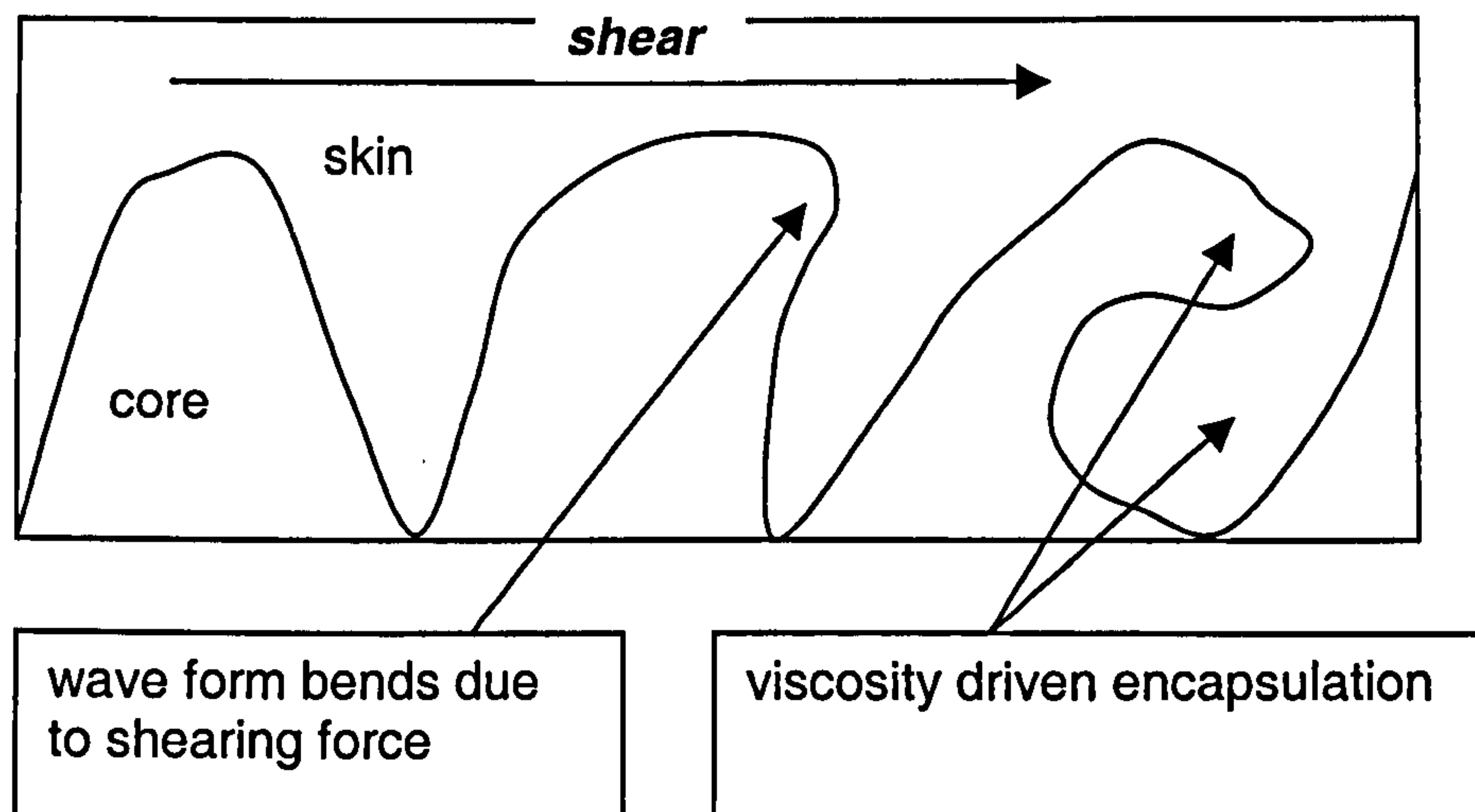


Figure 8-6 Development of mechanical hook

8.3.3 Origin of Oscillatory flow

It can now be postulated as to the origin of the oscillation at the interface, and how it might be related to the ridge effect. It has been seen that the pressure oscillation is linked to a particular range of injection speeds. This implies that there may be a critical speed at which onset will occur and there could also feasibly be a point at which it would stop. Injection speed produces increases in both shear stress and elasticity of the polymeric materials but filling progresses in a laminar manner, by pressure driven Poiseuille flow such as shown in Figure 8-7 until some critical point is reached.

The oscillation is not visible in the sprue of the moulding or generally around the gating area. Its absence in the sprue could be explained by the material being in 'pseudo' equilibrium in the sprue, but having two different

states of stress, one in each material. As the material exits the sprue into the mould the relaxation rates, pressures, and speeds are different. The obvious analogy here being the phenomenon of die swell in extrusion, which is only visible when the melt exits the die. Such swell is also employed in injection moulding to aid fountain flow as it provides adhesion of the melt onto the tool wall [Wilkinson, 1999]. In this case however there is not a single material 'swelling' but two. At a critical level of stress, a relaxation oscillation from one or both of these materials then causes periodic flow instability with dominant oscillations in velocity and pressure. In effect, this creates a self-excited oscillation even though it is propagated by a steady (non-periodic) source of energy, acting on both materials. The amplitude and frequency of the oscillation will depend on the mould geometry once the materials exit the sprue, the flow rate and the characteristics of the polymers themselves. With mixed material systems it is likely that the critical point of the onset of the oscillation will correspond to a critical difference in stress levels where elastic properties dominate over viscous properties in the melt. Further evidence to support this can be found in the literature. Cogswell [Cogswell,1996], states that in cone and plate rheometry when a material is subjected to a sinusoidal shear history, viscous and elastic responses have different phases. The elastic response to stress is sinusoidal, whilst viscous response is exactly $\pi/2$ out of phase. The change in dominance from a viscous regime to an elastic one would seem an extremely likely source of the oscillations in the materials seen in these studies.

According to Hooper, [Hooper, 1983] if the thin skin layer is less viscous, such as with in PA6 and PA12 skin material with a PP core, this effect would be stabilising. Hence the reason why there is no oscillation in this region, due to layer effects.

8.3.4 Layer Ratio

An effect can also be seen when the relative ratios of skin to core are varied. The results of surface assessments on both the PA12/PP system and the PS/HDPE system are shown in Tables 7-7 and 8-3. With the PA12/PP system when the proportion of skin was increased, the ridge effect also increased. This implies that reducing the size of the core component has a destabilizing effect on the interface. It has been shown in co-extrusion that if the more elastic fluid occupies less than half the channel it has a destabilizing effect [Chen, 1991]. It appears with co-injection in this particular case that it has caused a growth in the instability. This also appears to be true in the mouldings of PS /HDPE, however in this case we are looking at the peak to valley height of the styrene instability rather than the surface ridge. The reduction in the core component has caused an increase in the amplitude of the waveform in this case. These results imply that to successfully control the instabilities, the relative ratio of skin to core material is of the utmost importance.

8.3.5 From ridge to oscillation: instability growth

The appearance of the oscillation, like the ridge, is related to the increase in first normal stress difference at the interface between skin and core and the related elastic interaction. However whether the instability will grow or decay will depend on other factors. It would seem the ridge appears first, as normal stress differences occur at the wave front. However, at some critical value this leads to a growth in the instability, leading to wide scale oscillation along the interface. It has been postulated that this is related to the relative size of elastic to viscous forces, which produce the oscillation. Here also, the relative viscosities of the skin and core components will become important in controlling viscous encapsulation of any splitting waveforms. These waveforms are often termed bifurcations.

8.3.6 Bifurcations

Bifurcations are not unknown in polymer processing and are described by Cogswell [Cogswell, 1996] in co-extrusion. Bifurcations can even lead to droplet formation. Such as shown in Figure 8-8.

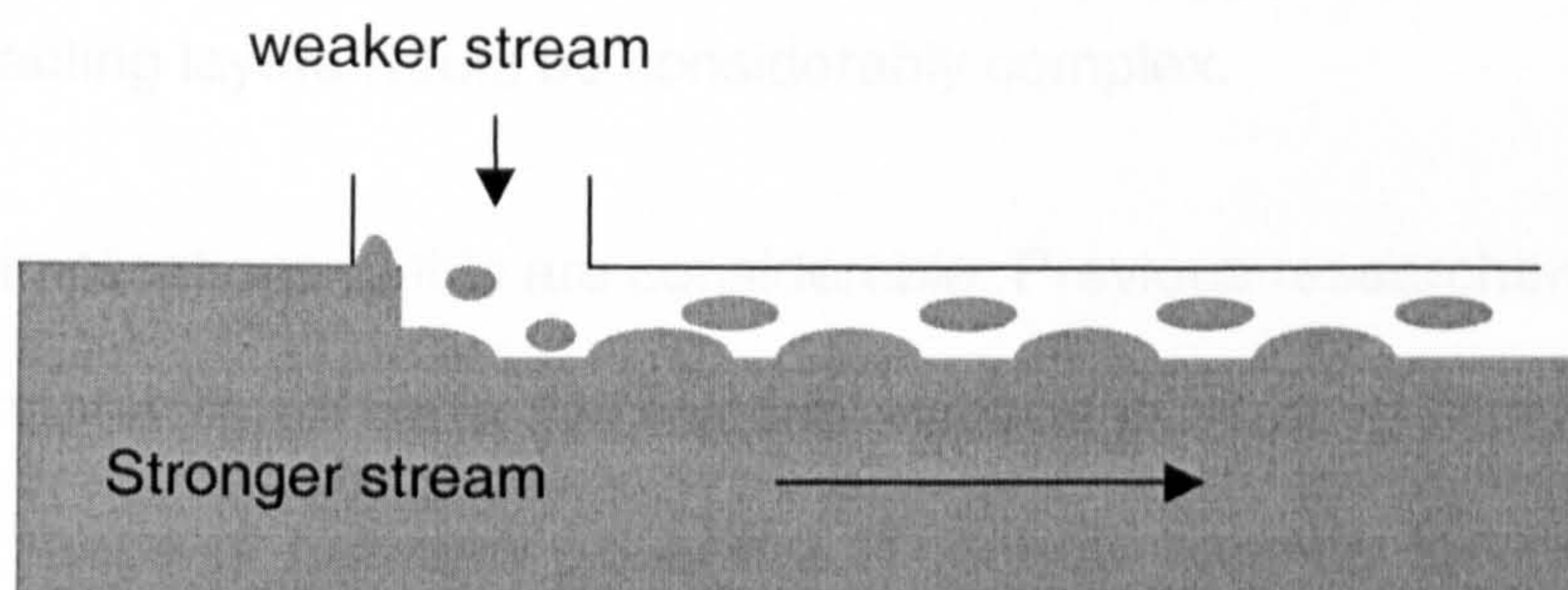


Figure 8-8 Droplet formation as a result of viscosity and velocity differences in extrusion [Cogswell, 1996]

Droplet formation was not seen in these experiments, but it is easy to see how encapsulation of the waveforms would lead to such effects. Any splitting of the waveform is accompanied by bending and elongation of the waves, caused by large shearing stresses, which are exerted at the wave peak or trough. It will move into material of the adjoining layer, which will have its own components of shear and velocity. It can be argued here that the amplitude of the waves and their spacing will affect the degree of bending. The volume of fluid contained in the peak or valley would affect both its ability to deform and the encapsulation mechanism. Another consideration is that high amplitude waves will affect layer ratios and vice-versa. As seen in section 8.3.4., this also appears to be of major importance. It was also mentioned earlier in the chapter that material in these peaks and troughs is likely to be orientated at different angles to the direction of flow. The effect will be as shown in Figure 7.2 and is likely to be reflected in the modulus and elongation properties as seen in previous experiments. It is likely that these effects will also have major implications for filling dynamics, as velocity and pressure gradients from the two interacting layers would be considerably complex.

The implications of this are considerable. Previous researchers as outlined in Chapter Three claim that material viscosities must be kept in a viscosity ratio range of between 0.5 and 2. This now appears too simplistic. For example, if one considers that gas assisted injection moulding is a variation of co-injection moulding and the effective viscosity of gas is zero, the viscosity ratio of materials in this case falls well outside that specified

and yet this technique is used commercially in a variety of commercial applications.

It is more likely that the relationship exists not between the viscosity of the two materials themselves, but between the viscosity of the more viscous fluid and the velocity of the core component. Encapsulation phenomena dictate that a high viscosity in the core and high velocity will make for more viscous fingering. The velocity of the incoming core material is the key parameter for controlling both the interaction on the flow front of skin and core and the elastic properties that shape the stability of the system. The relative interfacial viscosity of the material at the interface, which is not necessarily the same as the material within the bulk of the flow, will also shape encapsulation of any bifurcation. The size of these bifurcations will affect mixing mechanics and control mechanical properties through the interlocking mechanism described in earlier sections.

8.3.7 Requirements for Generating Instabilities

From the research program, the following factors are implicated for the generation of instabilities:

- A difference in the first normal stress
- Rheology differences specifically the interfacial viscosity ratio
- Immiscibility or inhibition of diffusion/relaxation mechanisms

The level of instability to be affected by:

- Channel thickness and layer depth ratios
- Core speed relative to skin
- Shear in the gating area.
- Polymer relaxation time

8.3.8 Implications for multi-material moulding

Evidence from co-injection literature does not exist to support many of the theories postulated here. This has meant looking to other disciplines and processes such as co-extrusion or other phenomena such as melt fracture or die swell in order to find comparisons and explanations. However, many of the parameters identified and supported by experimental data are similar to those implicated in the formation of co-extrusion instabilities and have been related to this literature as appropriate. This suggests the methodology to be a valid one. Differences between co-injection moulding and these processes have also been highlighted where appropriate. Complex mechanisms and interactions have been revealed and explanations for their occurrence given. Important material considerations have also been uncovered, for example, the ratio of skin to core which can stabilize or destabilize a potential multi-material co-injection moulding application. The level of inherent elasticity in a material and the shear that it will be subject to are all important criteria for future developments in this area. This method uses standard co-injection

moulding machinery and removes the need for costly compatibilisers. Whilst compatibiliser technology offers interesting possibilities for future multi-material developments, the lack of inter-facial mixing with resultant surface defects plus the cost of the compatibiliser itself mean that a system that could induce interfacial mixing would be a more attractive alternative. Another area for which this research may have implications is the field of recycling. Since mechanical interlock is a physical rather than a chemical method to enable adhesion, recycling of components by grinding should de-bond easily and assist in more effective separation. Again, this offers advantages over compatibiliser technology for whilst compatibilisers produce materials chemically bound together, little is known about the recyclability of the compatibilisers themselves [Goodship, 2001, b], [La Mantia, 1999].

This research has begun the study of interfacial instabilities in co-injection moulding. Whilst these studies have provided a solid basis, much more work is needed before this novel potential application for co-injection moulding can be fully utilized.

Chapter 9. Conclusions

This thesis has described experiments in multi-material co-injection moulding. Three different material combinations were used to highlight the differences between mouldings consisting of compatible and non-compatible materials. Fundamentally, three things have been achieved:

1. The mechanisms, which produced the ridge effect, have been identified.
2. The means to eliminate the ridge have been discovered by controlling the co-injection moulding process variables.
3. A method has been developed by using this knowledge to both promote improved bonding between skin and core materials whilst at the same time eliminating ridge defects.

It is the author's belief that each of these three areas identified are novel.

It can also be concluded that:

- Interfacial instabilities can exist in all co-injection systems even when the skin and core are the same material.
- One indicator of such instability is a ridge at the surface of a moulding directly above the skin/core interface.
- The strength of chemical adhesion by compatibilisation, with some limited entanglements, was shown to be less than the strength of

bonds produced by diffusion and chain entanglements. This was the case even when the extent of interlocking was limited as occurs in the formation of weld-lines.

- The concept of controlling the interfacial mixing through the inducement and control of the turbulent flow was introduced and basic experiments on immiscible materials produced evidence, which supported the hypothesis for a mechanism of mechanical interlock.
- Non-miscible mouldings of polystyrene and high density polyethylene can be made to bond by inducing interfacial mixing through control of injection speeds. The surface defects previously seen in compatibilised mouldings were not present as the stresses were dissipated at the boundary, therefore solving the problem of ridge formation.
- Important parameters in instability formation and control were identified these being:
 - ❖ A difference in the first normal stress at the skin/core interface
 - ❖ Rheology differences specifically the interfacial viscosity ratio
 - ❖ Immiscibility or inhibition of diffusion/relaxation mechanisms
- The level of the resulting instability is affected by the channel thickness and layer depth ratios, the core speed relative to skin, the shear in the gating area and the polymer relaxation time.

Chapter 10. Further work

Much of the further work identified here stems from the areas of research that were opened up during the course of this investigation but were not crucial to the aims.

1. Examine further the skin thickness/ property relationships for co-injection mouldings.
 - For example are these results peculiar to this particular grade of PP?
 - Morphology/crystallinity studies. To find heating/cooling/shear effects.
 - Vary skin/core temperatures as per speed trials to look at effects of a temperature gradient in the skin and core.
 - Compare to the behaviour of other polymers such as polystyrene.
2. Identify how the molecular orientation within the material may be further utilised, for example, in combination with techniques such as SCORIM.
3. Further Investigate the interfacial shear layer development and its relationship to fountain flow and SCORIM.
4. Develop the mechanical interlock mechanism for immiscible moulding further as a viable alternative to the use of compatibilisers. This would include quantifying the bond strength between skin and core components.
5. Study filled systems; how does the interlock mechanism change if fillers such as talc or glass fibre are incorporated?

The following two suggestions look to investigate the wider implications for this research into two other areas of current research interest.

6. **Weld-lines:** Weld-lines also produce a characteristic bump, similar to the ridge effect. Can similar methods employed here to identify the mechanism behind ridge formation help improvements in weld-line elimination, for example by improved mixing at weld-lines by manipulating viscoelastic properties.
7. **Melt Fracture:** Investigate whether the oscillations and melt-fracture are related phenomena and whether this research can shed light on the hotly debated subject of the cause of polymer melt fracture which has been a topic of research interest for nearly fifty years.

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